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MEASUREMENTS OF TEMPERATURES ON THE INTERNATIONAL PRACTICAL TEMPERATURE SCALE

by

Mono M. Manna,

SUMMARY

The work described in the thesis was undertaken as part of a programme of research into the thermodynamic and transport properties of steam, and deals with two aspects of measurements of temperatures on the International Practical Temperature Scale.

1. In Section 1 the investigation deals with the reproducibility of Platinum: 10% Rhodium-Platinum thermocouples at the freezing and melting points of silver. The experiments are carried out with 5 thermocouples, 2 from Johnson, Matthey & Co. Ltd. and 3 from Baker Industries Ltd. Using appropriate techniques the plateaus, with a duration varying from 30 minutes to 45 minutes depending on the rate of freezing and melting, remain constant to within ± 0.07 μV (± 0.007°C) during freezing and ± 0.12 μV (± 0.012°C) during melting. The agreement between melts and freezes fall within ± 0.05 μV. The cooling curves show reasonably good flats and the melting curves show in most cases a steady rise of less than 0.01 μV/minute. The best thermocouple shows a reproducibility of the order of ± 0.09 μV; equivalent to ± 0.009°C over 4 freezes and ± 0.22 μV; equivalent to ± 0.022°C over 4 freezes and 3 melts. The factors limiting reproducibility are considered to be the electrical measurements, temperature conditions in the furnace containing

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the ingot and the homogeneity of the thermocouple wires. The presence of strain, original or required, appear to be the main cause of uncertainty.

2. Section 2 deals with the calibration of a Platinum: 10% Rhodium-Platinum thermocouple by direct comparison with a standard platinum resistance thermometer at or near 630.5°C. The vacuum furnace specially designed for this purpose takes about 3 hours to attain the above temperature and this temperature is maintained stable within ± 0.1°C during each run or experiment. The temperature distribution along the axis of the furnace is reasonably uniform at the centre (0.05°C over $2\frac{1}{2}$" length) where the sensing elements of the thermocouple and the resistance thermometer lie. The e.m.f. against the temperature curves show the same type of relationship for both the thermocouple and resistance thermometer. The calibrated e.m.f. values of the thermocouple from two runs lie within ± 0.1 μV; equivalent to ± 0.01°C, the same agreement being found from the resistance thermometer measurements.

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CONTENTS

INTRODUCTION

The work described in this thesis forms part of a programme of research on the properties of steam. For the measurement of both thermodynamic and transport properties, the measurement of temperature is of great importance since many properties depend largely on temperature. Although temperature is an important factor in the determination of such transport properties as viscosity and thermal conductivity, the scale to which observed temperatures are actually referred, is not a critical factor. However, in the case of the determination of thermodynamic properties there is a special need to be able to relate actual observations to the International Scale of Temperature and thence to the thermodynamic or absolute scale. The precise relation between these two scales is not internationally agreed, although, in due course, such agreement may be reached. At that time it will be possible to correct observations on the I.S.T. to the thermodynamic scale and in the case of precise and scientific work such a distinction may be important. Keenan (40) observes that it is not the difference between the two scales that is important but rather the ratio of the derivatives. Using Beattie's measured values he estimates the departure from unity of the ratio of derivatives as 1/2500 in the range 0°C to 400°C. Since some of the best calorimetric measurements (N.B.S.) are estimated to have an accuracy of 1 part in 2000 or better, the relationship between the two temperature scales could be important, especially at elevated temperatures (600°C → 1000°C) where a large discrepancy could occur.

Although it is not practical to make measurements directly on the thermodynamic scale, it is necessary to overcome this difficulty by relating the measurements to another scale which is internationally reproducible (I.P.S.T.), from which follows the need to establish a scale* (in Glasgow) the I.P.S.T. The work described herein is associated with this endeavour and deals with two aspects of the programme, namely,

(1) The reproducibility of platinum: 10% rhodium-platinum thermocouples at the silver point.

(2) Calibration of platinum: 10% rhodium-platinum thermocouple against the standard platinum resistance thermometer in the vicinity of the antimony point (630.5°C).

LIST OF SYMBOLS

Unless otherwise defined in the text, the symbols used here have the following meanings:-

A,B,C, a,b,c	Constants
L	Length
o.d.	Outer diameter
i.d.	Inner diameter
F	Freezing
M	Melting
e_{Ag}	Mean e.m.f. during each melt or freeze
Δt	Time range of each melt or freeze
Δe	Maximum or minimum deviation of e_{Ag} over Δt
R	Resistance
t	Temperature ^{o}C
T	Absolute temperature
μV	Microvolts
S	Entropy

LIST OF FIGURES AND GRAPHS

CHAPTER 1

1.1 REVIEW OF LETERATURE

The Thermodynamic Kelvin scale on which temperatures are designated as ^{o}K and denoted by the symbol T is recognised as the fundamental scale to which all temperature measurements are referred. The size of the degree Kelvin has been defined by fixing the thermodynamic temperature of the triple point of water at exactly 273.16^{o}K. (Tenth General Conference of Weights and Measures, 1954, Resolution 3).

The experimental difficulties encountered in the gas thermometric measurements of temperatures on the thermodynamic scale led to the adoption in 1927, by the Seventh General Conference of Weights and Measures representing 31 nations, of a practical scale that could easily and rapidly be used to calibrate scientific and industrial instruments. Slight refinements were incorporated into the scale in a revision adopted in 1948. This scale was intended to be as nearly as possible identical with the thermodynamic scale.

The scale presented under the new title "International Practical Scale of Temperature" adopted by the International Committee of Weights and Measures in May 1960, is only an amended edition of the 1948 scale, the numerical values of temperatures remaining the same as in 1948.

Temperatures on the International Practical Scale of Temperature of 1948 are expressed in degrees Celsius, designated

by °C or °C (Int. 1948). The present I.P.S.T. is based on six fixed and reproducible temperatures to which numerical values are assigned; and on formulae establishing the relation between the temperature and the indications of instruments calibrated by means of the values assigned to the six fixed points. These fixed points are defined by specified equilibrium states, under 1 standard atmospheric pressure, except for the triple point of water.

Basic fixed points of the International Practical Temperature Scale

The pressure is 1 standard atmosphere except for the triple point of water.

		Temperature °C (Int. 1948)
(a)	Temperature of equilibrium between liquid oxygen and its vapour (Oxygen point)	- 182.970
(b)	Temperature of equilibrium between ice, liquid water and its vapour (Triple point of water)	+ 0.010
(c)	Temperature of equilibrium between liquid-water and its vapour (Steam point)	100.000
(d)	Temperature of equilibrium between liquid-sulphur and its vapour (Sulphur point)*	444.600
(e)	Temperature of equilibrium between solid and liquid silver (Silver point)	960.8
(f)	Temperature of equilibrium between solid and liquid gold. (Gold point)	1063.0

* The freeezing point of zinc 419.505°C (Int. 1948) being more reproducible than the boiling point of sulphur and being substantial independent of pressure is currently used in place of sulphur point.

The last decimal place given for each of the values of the primary fixed points represents the degree of reproducibility of that fixed point.

The means available for interpolation divides the scale into four parts:-

(a) From $0^{\circ}C$ to the freezing point of antimony ($630.5^{\circ}C$) the platinum resistance thermometer is used and the temperature t is defined by the formula

$$R_t = R_o (1 + At + Bt^2)$$

relating resistance to temperature t, based on the ice point ($0^{\circ}C$), the steam point ($100^{\circ}C$) and the boiling point of sulphur.

(b) From the oxygen point to $0^{\circ}C$, the platinum resistance thermometer is also used and the temperature t is defined by

$$R_t = R_o \left[1 + At + Bt^2 + C (t - 100) t^3\right]$$

The constant C is determined from value of Rt at the oxygen point.

(c) From $630^{\circ}C$ to $1063^{\circ}C$ the interpolation instrument is the Platinum, 10% Rhodium-Platinum thermocouple and the temperature t is defined by

$$e = a + bt + ct^2$$

relating e.m.f. to temperature t, based on the antimony point, the silver point and the gold point of the hot junction of the thermocouple, cold junction being at the ice point $0^{\circ}C$.

The International Temperature Scale Criteria for the platinum: 10% rhodium-platinum thermocouple are

$$E_{Au} = 10,300\ \mu V \pm 50\ \mu V:$$

$$E_{Au} - E_{Ag} = 1,183\ \mu V + 0.158\ (E_{Au} - 103.0\ \mu V) \pm 4\ \mu V$$

$$E_{Au} - E_{630.5} = 4,766\ \mu V + 0.631\ (E_{Au} - 10,300\ \mu V) \pm 8\ \mu V$$

where E_{Au}, E_{Ag} and E_{Sb} are the e.m.f.'s in microvolts at the freezing points of gold, silver and antimony respectively.

(d) Above the gold point optical pyrometry is used and the temperature t is defined by

$$\frac{J_t}{JAu} = \frac{\exp\left[\frac{c_2}{\lambda(tAu + T_o)}\right] - 1}{\exp\left[\frac{c_2}{\lambda(t + T_o)}\right] - 1}$$

where J_t and JAu are the spectral concentrations at the temperature t and at the gold point tAu of the radiance of a blackbody at the wave-length .

c_2 the second radiation constant is 1.438 cm. degrees,

T_o the ice point temperature in ^oK is 273.15 degrees,

λ is the wave length of the visible spectrum.

The most significant differences in the above scale compared with the 1927 scale are that the silver point is defined as 960.8°C instead of 960.5°C; the value of c_2 is defined as 1.438 instead of 1.432 and the Planck Law of Radiation is used instead of the Wien Law. As a result of these differences the temperatures as defined by the 1948 scale are higher in the region between 630°C and 1063°C

than those of 1927 scale, maximum differences being 0.4°C at about 850°C and above 1063°C they are lower, progressing from 0°C at 1063°C to 1.6°C at 1400°C and 3.6°C at 1700°C.

1.2 Thermocouples

The study of thermoelectric phenomena began in 1821 with the discovery of Seebeck that an electric current flows continuously in a closed circuit of two dissimilar metals when the junctions of the metals are maintained at different temperatures. Further, in that same period, Peltier (42) and Thompson (43) showed the reversible relation that exists between heat absoprtion and current flow in the circuit. Much later, however, these discoveries were applied to the measurement of temperature.

As a result of a large number of investigat-ions of the thermoelectric circuit in which accurate measurements were made of the e.m.f., current and resistance, the three laws have been formulated.

(1) The law of the homogeneous circuit:- An electric current cannot be sustained in a circuit of a single homogeneous metal, however varied in section, by the application of heat alone.

(2) The law of intermediate metals:- The algebraic sum of the thermoelectric forces in a circuit composed of any number of dissimilar metals is zero; if all of the circuit is at uniform temperature.

(3) The law of successive or intermediate temperatures:-

The thermal e.m.f. developed by any thermocouple of homogeneous metals with its junctions at any two temperatures

at T_1 and T_3 is the algebraic sum of the e.m.f. of the thermocouple; with one junction at T_1 and the other at any other temperature T_2 and the e.m.f. of the same thermocouple with its junction at T_2 and T_3. Considering the thermocouple as a reversible heat engine and applying the laws of thermodynamics to the circuit, the following relation is derived (Ref. 31, p.186).

$$E = \int_{T_1}^{T_3} S \, dT$$

from which it follows that

$$E = \int_{T_1}^{T_2} S \, dT + \int_{T_2}^{T_3} S \, dT$$

This law is frequently invoked in the calibration of thermocouples and in the use of thermocouples for measuring temperatures. An alternative treatment may be used [Zemansky (39)] applying the methods of irreversible thermodynamics to establish the same equation.

In the laboratory the thermocouple is connected to the instrument by means of a copper lead as shown in Figure 1 below.

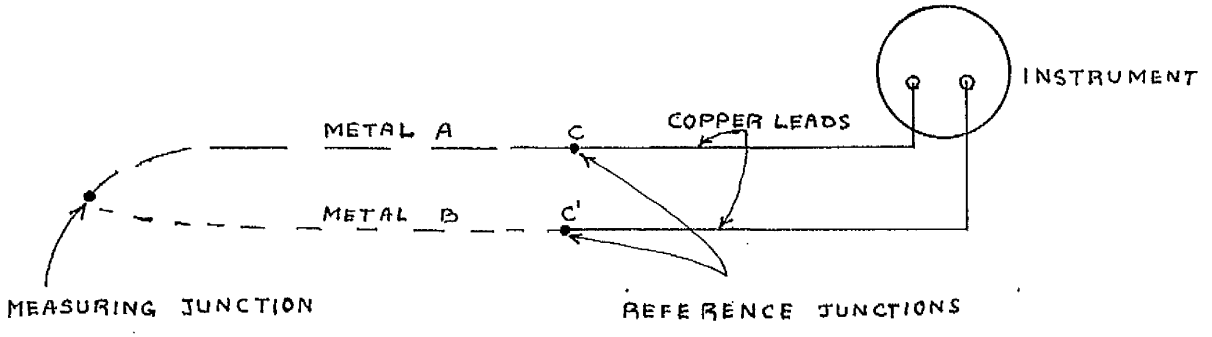


FIG. 1.

The reference junctions C and C^1 are maintained at the same temperature usually at 0^oC, the e.m.f. developed by the thermocouple is determined as a function of the temperature of the measuring junction. If the junctions C and C^1 are not maintained at the same temperature, the resultant thermal e.m.f. in the circuit will not only depend upon thermocouple materials and the temperature of the measuring junction, but also upon the temperature of these junctions and the thermoelectric properties of copper against each of the individual wires. Such a condition should be avoided.

Thermocouples provide many advantages as a means of measuring high temperatures. They take up little space and can be installed in restricted locations. They are easy to assemble and maintain and, because of their light-weight construction, offer distinct advantages in airborne applications. If the thermoelectric output is a non reversing e.m.f, it is readily subject to instrumentation. Further, in compatible atmosphere the thermal e.m.f. is a direct measure of the temperature and is not affected by environmental conditions. Barring contamination of the thermocouple metals, the expected error of a temperature reading can be stated with assurance.

On the other hand, for an ideal thermocouple wire the following features must be considered (1) high thermal e.m.f; (2) chemical and physical stability in the medium under measurement; (3) linearity in the relationship between temperature and e.m.f.; (4) negligible cold junction correction over the ambient temperature range encountered in service; (5) reproducibility of the e.m.f. characteristic from batch to batch; (6) ease of fabrication.

1.2(a) Platinum: Rhodium-Platinum Thermocouples

Platinum against rhodium-platinum alloys is a combination for thermocouples which has been in use for many years as standard practice for the accurate measurement of high temperatures. Platinum and its alloys are particularly suitable for this purpose because they have high melting points, are extremely resistant to oxidation at high temperatures and to chemical attack, and because they can be refined to a state of high purity. Other possible combinations of platinum metal and alloys generate thermal e.m.f. appreciably higher than that given by the platinum:rhodium-platinum thermocouple, but no other couple has been found to give equal stability and length of life over a wide range of temperature.

The two types in general use are those comprising pure platinum against either a 10 per cent or a 13 per cent rhodium-platinum alloy. The latter combination generates a slightly higher e.m.f. than the 10 per cent alloy. The physical properties of pure platinum and of the two rhodium-platinum alloys used for thermocouples are given below.

	Thermo pure platinum	10% Rhodium-platinum	13% Rhodium-platimum
Resistivity at 0°C, micro ohms centimeters	9.81	18.4	19.0
Resistance in ohms per yard (0.20 inch dia.) at 0°C	0.443	0.829	0.857
Mean temperature coefficient of resistance per 0°C (0 - 100°C)	0.00392	0.00166	0.00156
Thermal conductivity C.G.S. units	0.17	0.090	0.088
Ultimate tensile strength tons per sq. in. (annealed)	9	21	23
Elongation (annealed) per cent	40	30	30
Melting point	1769	1850 (Solidus)	1860 (Solidus)
Specific gravity	21.4	20.2	19.4

For continuous service a temperature of 1400°C is considered as a maximum but for intermittent work platinum: rhodium-platinum couples may be used up to 1600°C.

The reproducibility of the temperature - e.m.f. relationship of thermocouples depends upon the purity of the metals employed and the homogeneity of the alloy wire. Platinum, in respect of its thermoelectric characteristic, is extremely sensitive to the slightest amount of impurity and therefore a special grade known as "Thermopure" platinum is employed. The purity of this metal is measured by its temperature coefficient of resistance from 0°C to

$100^{o}C$, that is by the ratio

$$\frac{R_{100} - Ro}{100 \times Ro}$$

it being required that the value should be greater than 0.00392.

For rhodium

$$\frac{R_{100} - Ro}{100 \times Ro}$$ should be 0.00456.

Further much more serious errors can arise through contamination of thermocouples from outside sources and careful consideration should be given to the choice of sheath and its installation in order to prevent either errors in calibration or embrittlement of the wires. The useful life of a couple is in fact largely determined by the efficiency of its sheathing. Alumina sheaths have been found very satisfactory in service up to $1500^{o}C$.

1.2(b) Behaviour of Platinum: Platinum-Rhodium Thermocouples at High Temperatures

The effect of high temperatures on platinum: rhodium-platinum thermocuples was studied by McQuillan (1) in 1949; and it has been found that in air platinum and rhodium are lost by oxidation and volatalisation. To establish the amount of losses platinum-rhodium wires were heated electrically for long periods in air at a temperature of $1000^{o}C$. Losses were estimated by changes in weight and resistance measurements before and after heating. During 22 hours of heating in air the wires produced a thick black powder deposit and showed a weight loss of 10.3%. From the black powder

deposit, examined spectrographically, an appreciable quantity of rhodium was detected but the material was mainly platinum. It has been further observed by Jahn (2) that platinum oxidises twice as rapidly as rhodium in air and hence the loss of rhodium is also important enough to be considered.

Further it has been observed by McQuillan (1) that at any temperature the thermal e.m.f. developed by these thermocouples usually decrease after heating in air for a long time. This decrease in e.m.f. is considered to be due to the combined effect of loss of rhodium from the platinum-rhodium element and by diffusion of rhodium into the platinum wire. The thermal e.m.f. is also affected by the taking up or removal of impurities particularly in the platinum wire, the effect whether positive or negative depends on the nature of the impurities concerned. Since the rhodium content of the wire at the hot junction tends to increase as a result of oxidation, the observed decrease in thermal e.m.f. on prolonged heating must be due to the diffusion effect and the effect of impurities which together overcome the expected increase in thermal e.m.f. due to the increased rhodium content at the hot junction.

One thermocouple heated for 35 days at 800°C showed a decrease in e.m.f. of 26 μV at 1200°C and after heating at 1450°C the thermal e.m.f. of the couple was restored within 4 μV of its original value. It is assumed to be due to the formation of rhodium oxide on the surface of the wire at 1800°C, its subsequent dissociation

on heating at 1450°C, and the consequent restoration of the wire to its original composition. Hence one is led to the conclusion that the decrease in thermal e.m.f. after prolonged heating at a low temperature is due to the diffusion of rhodium from the platinum-rhodium element at the junction or due to the effect of impurities and that the recovery which occurs on heating is due to preferred oxidation of platinum, causing the rhodium concentration at the Junction to increase and thus producing an opposite effect which restores the resultant thermal effect.

Alumina, beryllia and carbon have been found by the above worker to have no contamination effect and could be used for the insulators of the thermocouples.

1.2 (c)

The effects of inhomogeneity of thermocouples and the state of strain in wires were observed by Selincourt (3). The lack of homogeneity in a thermocouple wire gives rise to a parasatic e.m.f., if associated with a temperature gradient; the effect being important in the region of the steep gradient leading to the hot junction. A wire exhibiting a uniform strain should have a good reproducibility in addition to showing no variation of e.m.f. when moved in a uniform temperature zone of the furnace; since the additional e.m.f. due to the strained condition of the wire would depend only on the temperature of the hot and cold junctions and so would form a constant addition to the total e.m.f. of the couple. Reannealing, when the strain removed partially or entirely would affect the total e.m.f. but

would not alter the reproducibility unless it introduced inhomogeneities into the wire . These were observed by moving the hot junction along the axis of the furnace. A wire exhibiting a non-uniform strain showed a poor reproducibility, since the parasatic e.m.f's arising in the non-uniform parts of the wire will depend on the temperature conditions in the neighbourhood, which may vary through the experiment as well as between different experiments under different conditions. Reannealing will affect the total parasatic e.m.f. by a general modification of the state of strain and in addition the magnitude of the parasatic e.m.f's due to the inhomogeneities will be reduced and hence reproducibility will be improved.

1.3 Electrical Resistance Thermometers

The resistance thermometer as an instrument for the precise measurement of temperature had its beginning with the publication in 1887 of H.L. Callendar's paper on the "Practical Measurement of Temperature". In 1887 C.W. Siemens (33) had outlined a method of temperature measurement by means of the platinum resistance thermometer or pyrometer. The basic principle is the change in electrical resistance of a conductor due to temperature. The conductor generally used is platinum. Since it, being a noble metal is more or less indifferent to its environment, is easily worked, and can be refined to have very little variation in temperature coefficient from batch to batch. An outstanding reason for the choice of platinum is, however, that the relation between resistance and temperature is a simple one, which holds over a very large range of temperature.

Resistance Temperature Formulae

For the temperature range between $0^{\circ}C$ and $630.5^{\circ}C$ as given in the definition of International Temperature Scale.

$$Rt = Ro \ (1 + At + Bt^2)$$

may be written in the Callendar form

$$t = \frac{1}{\alpha} \left(\frac{Rt}{Ro} - 1 \right) + \delta \left(\frac{t}{t_{100}} - 1 \right) \frac{t}{100}$$

where

$$\alpha = \frac{1}{t_{100}} \left(\frac{R_{100}}{Ro} - 1 \right) \text{ and } t_{100} = 100^{\circ}C.$$

The relations between the coefficients are:

$$A = \alpha\left(1 + \frac{\delta}{t_{100}}\right) \qquad \alpha = A + B\,t_{100}$$

$$B = -\frac{\alpha\,\delta}{t_{100}^{2}} \qquad \delta = -\frac{B\,t_{100}^{2}}{A + B\,t_{100}}$$

For the range $0^{\circ}C$ to the boiling point of oxygen as given in the definition of the scale.

$$Rt = Ro\left[1 + At + Bt^{2} + C\,(t - 100)\,t^{3}\right]$$

The relations between A, B and α, δ are the same as given above and the other relations are:

$$C = \frac{\alpha\beta}{t_{100}^{4}} \quad \text{and} \quad \beta = -\frac{C\,t_{100}^{4}}{A + B\,t_{100}}$$

In the thermometer the platinum is generally used in the form of wire of 0.1 mm. in diameter adjusted to have a resistance at $0^{\circ}C$ of about 25.0 ohms so that the resistance changes by about 0.1 ohm per degree Centigrade.

All resistance theremometers for accurate work are provided with four leads. They may take either of two forms. The original design of Callander has two leads to the bulb and a dummy pair of leads laid along side them. Measurements are made with Wheatstone Bridge with equal ratio arms and the dummy leads are placed in the opposite arm to the bulb coil. In this way, the errors due to changes in resistance of the leads are automatically compensated. The other type of thermometer, and generally for the most accurate

work, has two leads to each end of the bulb. The resistance may be measured by three methods: comparison with a standard resistance using a potentiometer; measurement either with a modified Wheatstone Bridge and commutator for the elimination of lead resistance or with a modified Kelvin double bridge.

Resistance thermometers are suitable for the measurement of temperature from - 240°C to 1000°C with an accuracy of 1°C. But for Science and Industrial use they are not recommended for temperatures above 630.5°C. It is known that the accuracy of reproduction of the temperature scale by means of a standard resistence thermometer in the range 0°C - 630.5°C varies between 0.005°C and 0.04°C in different sections of the scale. Above 630.5°C prolonged heating of platinum causes it to vaporise. With the very small diameter of platinum wire normally used for winding the sensitive element of a thermometer, the vaporisation leads to a quite appreciable change in its cross-section and thus interferes with the stability of the thermometer's characteristics. Further Strelkov (41) showed the vaporisation gradually covers the body of the sensitive element with a conducting film which by-passes the windings of the coil, and thus alters the calibration of the thermometer at high temperatures.

In spite of these difficulties, the meteorological advantage of the resistance thermometer over the thermocouples has led to its use for temperature measurements in the "thermo-electric" section of the scale (630 - 1063°C) using an instrument of special design.

PART I

PREFACE

The first section gives the results of an investigation into the reproducibility of platinum, 10% rhodium-platinum thermocouples at the freezing and melting points of silver. The accuracy of the measurements for reproducibility is considered to be limited by (1) the thermo-electric homogeneity and stability of materials forming the thermocouple, (2) the temperature distribution in the furnace containing the ingot and (3) the accuracy of the electrical measurements. The state of strain and contamination of the thermocouple wires were found to be the main sources of errors and it was difficult to attain a temperature distribution along the axis of the ingot better than 0.1 μV/cm. (0.01°C/cm). The accuracy of the electrical measurement was of the order of $\pm$ 0.01 μV (0.001°C). Considering all these factors the expected reproducibility from the freezes is of the order of $\pm$ 0.1 μV ($\pm$ 0.01°C)

CHAPTER 2

RESULTS OF EARLIER WORKERS ON SILVER POINT

2.1 Several investigations on the gold and silver points were made in the early period of development of the gas thermometry. The most precise ones are those by Holborn and Day (4) in 1901; and Day and Sosman (5) in 1910. The gold and silver points were shown by Holborn and Day to be 1063.5°C and 961.5°C respectively with an accuracy ± 0.8°C. The values in the measurements by Day and Sosman were 1062.4°C and 960.0°C respectively with an accuracy the same as that of Holborn and Day.

2.2 Selincourt (3) investigated in 1939 the reproducibility of Platinum: 10% rhodium-platinum thermocouples at the freezing points of gold, silver and antimony. The observations using an ingot showed that with gold, during freezing and melting, the readings remained constant to ± 0.1 μV and the agreement between melts and freezes also fell within this limit. With silver, the cooling curves did not show good "flats" and in particular the melts were not reliable, in which case there was a steady rise of about 0.1 μV per minute. In the case of antimony, it was not possible to obtain a melting curve with a slower than about 0.9 μV/min. and the calibrations were confined to freezing points. Further, owing to the very large undercool exhibited by this metal, the flat portion of the cooling curves after the undercool were in general very short.

The best thermocouples selected from a large number calibrated, gave reproducibilities of the order of ± 0.05 μV (3M, 2F) for gold, ± 0.1 μV (4F) for silver and ± 0.1 μV (4F) for antimony: in brackets, the number of metls and freezes are taken into account. Other inferior thermocouples showed a continuous fall of 4.8 μV in the case of 12 successive calibrations at the silver point. One couple which had first shown at the silver point a high constancy (agreeing to ± 0.1 μV over 2 freezes), developed later variations (agreeing to ± 0.2 μV over 4 freezes but with a mean value 2.0 μV below the former value).

2.3 C.R. Barber (6) published in 1950 the results of his e.m.f temperature calibration of 12 platinum: 10% rhodium-platinum thermocouples, six from each of two manufacturers, over the range from 0°C to 1760°C. At the freezing point of silver, using a silver ingot, observation was made on each of 12 thermocouples in turn. The reporducibility of the e.m.f. of the thermocouples from one freeze of silver to another was within 1 microvolt, equivalent to better than 0.1°C. The uniform temperature condition along the axis of the ingot was given to be 0.2 microvolts/2 cm. The departures in e.m.f. of the couples of each make from their own means was shown to be within ± 0.5 μV at the silver point and the accuracy of the measurements was estimated to be ± 0.1°C up to 1063°C.

The results of interpolated values obtained by using the quadratic equation $e = a + bt + ct^2$, and based on the e.m.f. values at the freezing points of antimony, silver and gold, were compared

with those found by measuring with platinum: 10% rhodium-platinum thermocouple at the same temperatures. It was shown that at the temperatures of 750°C, 800°C and 850°C the interpolated values were in excess of the values obtained by measuring with the thermocouple by only 1.1 and 2 μV respectively. Thus Barber showed that platinum: 10% rhodium-platinum thermocouple is a suitable standard instrument for realising the international temperature scale over the range 630°C to 1063°C.

2.4 On the Thermodynamic Temperature Scale, Oishi, Awano and Mochizuki (7) determined, in 1955 using gas thermometer in conjunction with platinum: 10% rhodium-platinum thermocouple, the temperature of gold and silver points. For a constant volume gas thermometer enclosing a definite mass of gas, the temperature T on the Kelvin scale is determined from the relation

$$T = T_o \frac{p_t}{p_o} \frac{1 + \lambda t + T_v/[V_{op}]_p = 0.76 \sum_{n'=1}^{n'} Vn'/T'_{vn'}}{1 + \mu(p_o - 0.76) + T_{vo}/[V_{op}]_p = 0.76 \sum_{n=1}^{n} v_n/T_{bn}} - F_t$$

The derivation of this equation is explained in the paper of the above authors.

Difference of temperatures in the neighbourhood of the gold or silver point was determined by a standard thermocouple, for which the temperature-e.m.f. relation is expressed by the equation

$$e = a + bt + ot^2$$

when from the characteristic of a thermocouple the following relations are derived

$$T_{Au} - T = t_{Au} - t = (e_{Au} - e_t) \times 0.0853$$

$$\text{or } T_{Ag} - T = t_{Ag} - t = (e_{Ag} - e_t) \times 0.0876$$

for a temperature near the gold or silver point respectively. Where e_{Au}, e_{Ag} and e_t are the e.m.f.'s at the gold point t_{Au}, the silver point t_{Ag} and a temperature t near t_{Au} or t_{Ag} respectively, t being in ^{o}C. Therefore T_{Au} or T_{Ag} on the Thermodynamic Temperature Scale can be determined from the gas thermometric measurements at temperature T near the gold and silver points respectively.

The result of measurements taken over 3 months showed the mean value of T_{Ag} to be 1234.430^{o}K (961.280^{o}C) with standard mean deviation of 0.038^{o}C and that of T_{Au} to be 1336.836^{o}K (1063.680^{o}C) with the standard mean deviation of 0.036^{o}C. Further, using a silver ingot the reproducibility of thermocouples at the silver point was shown to be 0.5 microvolts from the cooling curves.

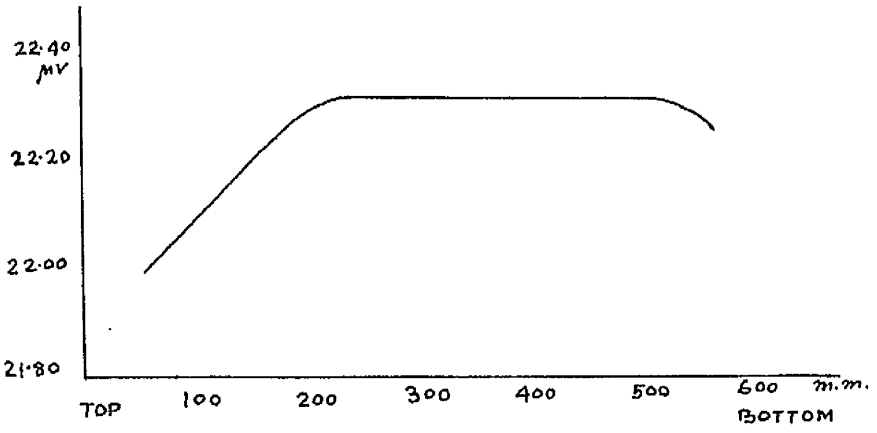
2.5 Further gas thermometric determination of the temperature of gold and silver points was carried out by Moser, Otto and Thomas (8) in 1958 and the values were shown to be 1064.76^{o}C and 962.16^{o}C respectively.

CHAPTER 3

APPARATUS

3.1(a) Design of the Furnace

The furnace used is essentially similar in design to that used by De Selincourt (3), but with some modifications as detailed in Figure 1. It is a vertical cylindrical furnace with the heater wound uniformly on a high thermal shock resistant 10A material tube whose conductivity is much higher than that of the insulation (alumina powder) used in the body of the furnace. To increase the uniform temperature zone, the central portion of the furnace tube is occupied by a heavy Nickel block ($10\frac{1}{2}$"L x $4\frac{9}{16}$" o.d. x $3\frac{1}{8}$" i.d.). The nickel block, though of low conductivity, has the advantage that it deteriorates by oxidation and a hard crust of oxide is formed which protects the remainder of the metal. The ends of the tube were fitted with blocks of low conductivity refractory material, e.g. fire-bricks to prevent direct heat loss from the ingot to the atmosphere. The bottom of the furnace tube was closed to prevent the natural convectional flow of air. For such a furnace the distribution of temperature along the axis as described by Alieva (9) is shown in the graph below.



It is seen from the graph that uniform temperature zone extends more towards the bottom and that the maximum heat loss occurs at the top. In the finally assembled state the silver ingot was 5" away from the bottom and 11" from the top of the furnace of 20" total length, so that the whole length of the ingot would be in the more uniform temperature zone.

3.1(b) Heaters

A Nicrome ribbon 1/8" width x 0.0142" thick (Tophet A) was used for the main heater and two supplementary windings 26 s.w.g. (Brightray C) threaded through alumina bead insulators were provided at each end of the nickel block to compensate the heat losses at either ends of the furnace tube. Two thermocouples T_1 and T_2 measure the temperatures at the two ends of the ingot and the power supplied to the two supplementary windings could be adjusted to make T_1 and T_2 as nearly equal as possible. In view of the poorer insulating properties of the refractories at high temperature there might be considerable leakage from the mains to

any earth available in the thermocouple circuit, and to reduce this alternating current was used for heating the furnace.

3.1(c) The silver ingot was 4" long, 1½" in outer diameter and ½" in inner diameter allowing an immersion of the thermocouple well of 3½". The ingot was contained in a graphite crucible and as silver absorbs oxygen in the molten condition and then shows a considerable depression of the freezing point, the surface of the ingot was covered with graphite powder to a depth of ½" to avoid oxidation. The thermocouple well was a thin graphite sheath made as an integral part of the graphite crucible lid serving to protect the thermocouple from being contaminated by the silver. Temperature distribution over the length of the ingot was also improved by the use of a substantial block of graphite for the crucible. The crucible was formed by boring an axial hole of 1½" diameter in a cylinder about 2.75" diameter and 5⅝" long, the details being shown in Figure 1. The crucible was contained in a high thermal shock resistant alumina (10A material) tube which extends 2" above the top of the furnace, thus providing a means for removing the crucible from the furnace. Alumina powdex insulation filled this tube from the top of the crucible to the level of the top of this tube. An outer silica tube (A) was used so that no alumina powder could fall into the thermocouple wall. To indicate the correct position of the thermocouple hot junction and also to measure the temperature gradient along the axis of the ingot a gear drive was set up, as shown in Figure 4; in order to permit the thermocouple sheath to be moved vertically.

Two thermocouples made of 30 s.w.g. wire and 6 ft. in length supplied by Johnson, Matthey & Co. Ltd. and three others of the same gauge supplied by Baker Industries Ltd. were used to measure the reproducibility. They were threaded through twin-bore alumina insulators, 80 cm. long, 4 mm. in diameter and with 1 mm. bore. The remainder of the wire to the cold junction was insulated with P.V.C. sheaths, and to prevent the formation of an inductive loop, the two arms were bonded together. During the threading of long lengths of wires through the narrow holes in the insulators it was quite possible to produce strains on the wires. To get rid of the strain as far as possible all the couples were annealed electrically for 1½ hours at a temperature of about 1350°C after they were threaded in their insulators.

The leads from the thermocouple to the measuring potentiometer were 24 s.w.g. copper wires insulated with P.V.C. sheaths. This would not produce any parasatic e.m.f. between the thermocouple junction and the measuring potentiometer and also heat conduction would not be enough to affect the temperature of the cold junction.

3.2 Triple Point Cells

For very accurate determination of the reproducibility of the thermocouples it is necessary that the cold junctions are always at a constant temperature. It is found by other investigators that the temperature of the triple-point of water , the temperature at which pure ice, liquid water and water vapour are in equilibrium,

can be realised more readily and accurately than can the ice-point. The difference is considered to be due to the effect of pressure and the effect of dissolved gases. The temperature of the triple-point of water is realised in sealed glass cells containing only water of high purity. These cells have an axial re-entrant tube for the thermometer. In such cells the triple point temperature is obtained whenever the ice is in equilibrium with a liquid-vapour surface. At a depth h below the liquid-vapour surface, the equilibrium temperature, t, between ice and liquid water is given by the formula

$$t = 0.01^{\circ}C - (0.7 \times 10^{-6} \text{ deg/mm})\ h.$$

With a good triple-point cell, the triple-point temperature of water, $0.01^{\circ}C$, can be reproduced with little difficulty to within $\pm\ 0.0001^{\circ}C$. Therefore the cold junctions of the thermocouples were kept at the triple-point of water.

Preparation and Use of the Cells

Two triple-point cells have been made by the author in this laboratory. The same method as used at N.P.L. was followed for the construction of the "pyrex" cells, (The details are shown in Fig. 2) for cleaning, filling with double distilled water and sealing under vacuum. Approximately 10 litres of water was distilled through each column before they were used to steam and charge the cells. But the sealing at this upper joint was followed slightly differently than it was suggested by N.P.L. The suction was applied through the joint at A with the cell held vertical and the cell was then warmed over the whole surface by waving a luminous bunsen flame for the removal

of air from water and the glass walls. When the water level in the cell was lowered by about 1" due to evaporation, the tap between the cell and the pump was closed, but the vacuum pump was still kept running in case there was any leakage of air through the joint at A. After 5 minutes, when there was no more boiling of water and water inside the cell was steady, the cell was sealed off by collapsing the constriction with a very fine torch or bunsen flame and then drawing off. After cooling down to room temperature the cell was found on inverting to give a good "water hammer" effect.

Cell No. 1 was cleaned and filled with double distilled water, but 5 days later during the formation of an ice sheath for the second time, leakage of air was found through the joint of the wall with the main body of the cell. This might be due to the fact that stress relief of the joint made by the glass blower was not perfect. However Cell No. 2 was first cleaned with demineralised water for 14 hours and with double-distilled water for the last 4 hours, but was filled completely with double distilled water.

The Cell No. 2 was compared with a standard cell obtained from the Chemistry Department of the University. The two cells were first of all cooled for an hour in two large Dewar flasks containing melting ice. A sheath of ice several millimeters thick was formed round the thermometer wall by the circulation of cold methanol from a methanol/solid CO_2 freezing mixture passing through it. Here the gas liberated from the subliming CO_2 was not allowed to escape freely into the atmosphere and the pressure consequently built up was used to

force the methanol through the apparatus. The well was then emptied and water at room temperature was added to melt a thin layer of the ice nearest to the well. When the ice-sheath was free from the well, ice-cold water was added taking care that no particles of ice found their way into the well, since a particle of ice would take a considerable time to melt due to the small difference of temperature 0.01°C between the ice and triple point temperature.

Every day the cells were covered up to the top with ice in a Dewar Flask and with the top carefully protected it was possible to hold the triple-point temperature for about 8 days.

The two cells were compared by measuring the resistances of a Barber design resistance thermometer held inside the wells, (about 1" away from the bottom of the well), using a Smith Bridge and galvanometer photocell amplifier unit. A fine thermostat added to the bath heater circuit of the bridge helped to keep the bath permanently at 25.5°C ± 0.5°C.

3.3 Electrical Measurements

The equipment for electrical measurement and control and the furnace was situated in a temperature controlled (± 1.5°C) laboratory. The electrical circuit diagram is shown in Figure 3. The measuring instrument used is a very high precision type 5205-A/Auto current controller potentiometer supplied by H. Tinsley & Co. Ltd. This potentiometer is designed to be nearly free from parasatic thermal e.m.f. A galvanometer of adequate sensitivity (Tinsley type 5214 photocell galvanometer amplifier with type MS.2.45.E

galvanometer and type 5214A thermal compensator) was connected to the galvenometer terminals. The thermal compensator is provided with a "Galvanometer Series Resistance" control. The circuits of which voltages are to be measured, were connected to the pairs of terminals "1", "2", "3" or "4".

The controller driving a d.c. current control system consists of a high gain d.c. amplifier. ~~The~~The e.m.f. of a standard cell is compared with the voltage drop across a resistance in the current or standardising circuit, the difference, or error, is fed into the d.c. amplifier which causes the current to change in the direction which reduces the error. This error under steady state conditions will be less than 1 part in 10^6.

During switching the small amount of energy absorbed by the galvanometer produces a small variation of e.m.f. of the order of 10 parts in 10^6, but it reduces to one or two parts within few minutes. Fluctuations in voltage supply for the lamps cause transients in the stabilised current supply which gives rise to errors. Vibrations also produce a similar effect. The drifting of the stabilised current is usually caused by the thermal e.m.f's in the standardising circuit or standard cell circuit. The temperature coefficient of standard cell being 40 parts in $10^6/^oC$, it was necessary with high precision measurements to control the temperature of the standard cell to close limits and in the temperature controlled laboratory the temperature of the cell 5312A type was controlled within $\pm$ 0.05^oC.

The electrical measurements were found quite satisfactory to well within the limits required, being limited by the galvanometer sensitivity which gives a deflection of 1 cm/0.1μV.

CHAPTER 4

EXPERIMENTAL TECHNIQUES

The accuracy to which the reproducibility of the thermocouples can be realised depends mainly on two factors:

(a) the freezing point of the actual specimen of silver employed, and

(b) the precision with which the calibration of the thermocouples can be reproduced.

The impurity of a silver ingot supplied by Johnson, Matthey & Co. Ltd. is claimed to be 10 p.p.m. and the following procedures in the method of calibration are recommended in the specification of the international Temperature Scale:

(1) The thermocouple should be immersed in the specimen through a hole in the centre of the crucible cover and during freezing the metal should be cooled slowly from a temperature a few degrees above its melting point.

(2) The couple should be mounted in a twin-bore alumina tube thus separating the two wires.

(3) The immersion of the couple inside the specimen should be such that during the period of freezing and melting the couple can be lowered or raised about 1 cm. from its normal position and the e.m.f. indicated by the thermocouple should not alter more than 1 μV (0.1^{o}C).

(4) During melting and freezing the e.m.f. should remain constant within 0.1 μV (0.1°C) for a period of at least 5 minutes.

(5) Melting and freezing should not differ by more than 2 μV (0.2°C)

Before putting it inside the furnace the surface of the silver ingot was cleaned and the metal was handled carefully to minimise contamination. Work was carried out with the metal contained in a graphite crucible, the top surface being covered with graphite powder. Though solid silver does not oxidise readily it is necessary to protect it from oxygen during a freezing point determination. Since it absorbes oxygen in the molten condition and then shows a marked depression of the freezing point due to emission of oxygen during solidification. But absorption of oxygen from the air does not take place until 30° above the melting point, so care was taken not to heat the metal more than it was necessary. Thermal analysis was carried out under a certain cooling and heating rates. Temperature changes in the melt before transformation was during melting about 1.5 μV/min (0.15°C/min) and during freezing about 0.8 μV/min (0.08°C/min). With the melt held a few degrees from the transformation temperature, the furnace power was adjusted to give a desired rate of cooling or heating.

CHAPTER 5

5.1 DISCUSSION OF EXPERIMENTAL RESULTS

5.1(a) Triple Point Cell

The results of the comparison between cell No. 2 and the Chemistry Department cell obtained over a period of 9 days are shown in the Tables 1 and 2 and the graph plotted is shown in graph No. 1. It may be seen that in the first day the temperature of both cells rose by amounts corresponding to 4×10^{-6} ohms, which is approximately 4×10^{-5}°C. The pronounced lowering of the temperature by 2×10^{-4}°C on the second day was presumably due to an increase in strains which would occur with relatively rapid freezing. Later on the slow rise in temperature is believed to be associated with the crystal growth and release of strains in the ice. The two cells, however, agreed with each other to within $\pm 2 \times 10^{-5}$°C. The reproducibility of cell No. 2 was found to be better than that of the Chemistry Department and lies within $\pm 1 \times 10^{-5}$ ohms which is approximately $\pm 1 \times 10^{-4}$°C. The overall small changes in the readings of the two cells under comparison might be accounted for by actual changes in the temperature of the cells, by changes in the resistance of thermometer or by changes in the measuring bridge.

5.1(b) Results of Calibration at the Silver Point

The melting and freezing curves obtained with 5 thermocouples, reannealed after threading through their insulators are shown in graphs Nos. 2,3,4,5 and 6. An upward displacement of the thermocouple along the axis during melting or freezing produced no greater change than 0.1 μV/cm of movement.

Cooling curves show the rise from supercool (recalescence) to a plateau and an alloy slope. During the period of recalescence, nucleation and growth of the solid occurs at such a low rate that the amount of latent heat of fusion released is insufficient to balance the heat lost to the rest of the furnace. Afterwards the growth rate becomes great enough to overcome this loss and the temperature of the melt steadily increases. Eventually the melt temperature becomes constant. The last section of a freezing curve is a long alloy slope of decreasing temperature which persists until all the metal is solid. The rounding at the end of a freezing curve is due to both a rapidly increasing concentration of dissolved solute in the newly frozen solid and to the increasing rate of heat loss from the melt as the furnace block drops well below the melt temperature.

The melting curves show the rounding at the end a few minutes prior to the liquid break. This may be due to convection currents in the crucible when the bulk of the sample is liquid and only a small fraction of the change is still solid.

The ideal range of alloy transformation temperatures is the difference in the temperatures at which melting or freezing

begins and ends in a completely homogenised alloy or, in other words the difference in the temperatures of the solidus and liquidus for the alloy on the equilibrium diagram. In practice great obstacles exist in realising ideal melting ranges because it is difficult to attain complete homogenisation of a sample; this is a consequence of the differences in the solubilities of the impurities in the solid and liquid alloys and of low rate of diffusion of the solute in the solid.

In general, the observation showed that the plateaus, with a duration varying from 30 minutes to 45 minutes depending on the rate of freezing and melting remained constant to within ± 0.07 μV during freezing and ± 0.12 μV during melting. The agreement between melts and freezes fell within ±0.05 μV. The cooling curves, as seen from the specimen curves, show quite good flats. On the melting curves the plateaus are not as constant in temperature as the freezing plateaus but show in most cases a steady rise of less than 0.01 μV/min., and hence the melts show a reproducibility some tenfold better than that obtained by the earlier workers.

The calibration figures obtained for 5 thermocouples are set out in Tables 4,5,6,7 and 8. The couples No. 1 and No. 2 were supplied by Johnson, Matthey & Co. Ltd. The couple No. 1 first gave 2 melts (Table 4A) agreeing to ± 0.15 μV and 2 freezes agreeing to ± 0.08 μV, the overall agreement of 2 freezes and 2 melts being ± 0.16 μV. Then the thermocouple was replaced inside the furnace after several days during which the voltage stabiliser

was not working properly. This time the couple showed a continuous fall of 0.3 μV in the course of 3 freezes and the agreement between one freeze and its previous melt was 0.5 μV. This poor result is to be attributed mainly to small strains which may develop in the wire due to normal handling during replacement. After 1 month, during which the work was carried out with other thermocouples, the couple was reannealed when the agreement among 2 freezes and 1 melt was found (Table 4c) to be ± 0.18 μV, but with a mean value as much as 2.0 μV below the former value. Further before and after reannealing the reproducibility of each melt or freeze was found to be the same and therefore showed that the wires exhibited a uniform strain which changed only the total e.m.f. of the couple after reannealing.

Couple No. 2 gave (Table 5A) 4 freezes agreeing among themselves to ± 0.09 μV and 3 melts agreeing to ± 0.12 μV, the overall agreement among 4 freezes and 3 melts coming within ± 0.22 μV. The departure in the mean e.m.f. of couple No. 2 from that of couple No. 1 is 0.52 μV. After one month, during which the silver ingot was melted and solidified about 20 times, the couple No. 2 was tested again and gave (Table 5A) 2 freezes and 2 melts coming within ± 0.15 μV with the mean value only 0.14 μV below the former value and hence shows that during this period the silver point has not changed considerably.

Couple No. 3, No. 4 and No. 5 were supplied by Baker Platinum Ltd. These three couples behaved nearly the same in showing their

changes in e.m.f. values from one freeze to another freeze and also from one melt to another melt, the average agreement between one freeze and its previous melt being 0.8 μV. Couples No. 3, No. 4 and No. 5 gave (Tables 6,7 and 8) 4 freezes and 3 melts agreeing to ± 0.23 μV, ± 0.28 μV and ± 0.28 μV respectively. The departures in mean e.m.f. of couple No. 3 from that of couple No. 4 and couple No. 5 are + 5.92 μV and - 1.68 μV respectively.

In general, it is seen from the results that each thermocouple has a tendency to show a continuous fall of its reading in the course of successive calibrations. This decrease in thermal e.m.f. on prolonged heating might be affected by the diffusion of rhodium from the platinum-rhodium element at the hot junction, or by the taking up or removal of impurities in the thermocouple wire. Also this decrease might be affected by the small strains due to slight movement of the element wires of a couple relative to the insulators and to the differential expansion of the wires and the insulators, when they are placed in the furnace. Since the space available is restricted, this movement gives rise to friction between the thermocouple wires and the walls of the insulator and also if the wires become jammed at any point, to tension or bending, according to the direction of the relative movement. Such strains undergo reannealing on prolonged immersion in the furnace and may thus give rise to gradual modification of calibration.

As all these results were obtained with the same furnace the different reproducibility shown by the couples of different make is to be attributed to different purity or in-homogeneity of the element wires.

5.2 Conclusions

The above experiments suggest that using high grade equipment the practical limit in the precision reproducibility determination of a platinum:10% rhodium-platinum thermocouple is of the order of ± 0.09 μV equivalent to ± 0.009°C (4F) and ± 0.22 μV equivalent to ± 0.022°C (4F, 3M). the symbols in brackets refer to the number of freezes and melts taken into account. Further, the melts are quite reliable enough to be taken into account, i.e. there is as well an increase in the accuracy over that obtained by earlier workers. The above calibration figure is for the couple selected as being the best of all couples tested by the author in this laboratory. The main difficulty in attaining the above accuracy lies in getting sufficiently homogeneous and pure wire for the thermocouple. The presence of strain, original or acquired accidently by normal handling of the thermocouples in course of measurement, and gradual contamination of the wires during heating are believed to be the main causes of uncertainties.

The limitations placed on the reproducibility measurement by the potentiometer, the triple point cell and the thermocouples combine to form a formidable barrier to any further improvement in the precision.

PART II

PREFACE

This section describes the calibration of a platinum; 10% rhodium-platinum thermocouple by direct comparison with a standard platinum resistance thermometer in the vicinity of the antimony point (630.5°C). This temperature is the transition from resistance thermometric measurements to thermocouple measurements on the I.P.S.T. For calibration a bath of stirred liquid is usually used to attain a temperature ranging from -80°C to 630.5°C within the limits of accuracy of the test. But such baths take a long time to attain an elevated temperature near 630.5°C and the purpose of using a vacuum furnace is to get the temperature in much quicker time and stable within the limits of accuracy of the test. The furnace specially designed for this purpose takes about 3 hours to attain a temperature near 630.5°C and this temperature is maintained stable within ± 0.1°C during each run on experiment. The calibrated e.m.f. value of the thermocouple at 630.536 ± 0.0157°C, based on resistance thermometric measurement is 5543.1 ± 0.1 μ V.

CHAPTER 6

6.1 APPARATUS

The design of the apparatus is shown in detail in Figure 5. It is a vertical cylindrical furnace maintained at a vacuum by connecting a gas ballast rotary high vacuum pump through joint A. Thin cylindrical copper radiation shields were used rather than powdered thermal insulation to minimise degassing. The furnace body was surrounded by a steam jacket to maintain a constant temperature at the outside and also to reduce heavy heat losses from the inside. The steam used in the jacket was passed through a condenser and the water condensed was fed back to the electrothermal boiler (Figure 6B).

Three windings made of Nichrome ribbon were used for the heater and these were wound uniformly round six alumina rods. The voltage supplied to all the three windings could be separately controlled by variable rheostats. The supply is from 3KVA Sorensen voltage regulator which stabilises the input voltage to the furnace to within 0.2%. To increase the uniform temperature zone of the furnace, the central portion of the furnace was occupied by a 17" long copper rod of 1" diameter so as to equalise the temperature by conduction.

Two central holes were drilled into the copper rod from either end, the top one was for the thermocouple pocket and the bottom one was for the resistance thermometer pocket. The pockets were made of stainless steel tubes with one end closed and the open ends were silver soldered to the end flanges of the furnace.

Six Pyrotenax thermoelectric cables (nichel chromium/ nickel aluminium thermocouples) were used for measuring the temperature. These were placed with a regular spacing of $2\frac{1}{2}$" along the length of the copper block such that when the apparatus was assembled the ends of the thermocouple and resistance thermometer pockets lay in the centre of $2\frac{1}{2}$" length covered by the thermocouples T_3 and T_4. The thermocouples were also silver soldered to the end flanges; during this period the thermocouples No. 2 and No. 5 were burnt out and there were only four thermocouples left to determine the vertical temperature gradient along the heating zone of the furnace. By varying the power supplied to the coils it was possible to achieve a temperature distribution of better than 2 V (0.05°C) over the centre $2\frac{1}{2}$" of the furnace at temperature 630.536°C. The maximum vacuum obtained inside the furnace is of the order of 0.9 mm. of Hg. This relatively poor vacuum might be due to the degassing from the cement used for covering the windings and from the wall of the furnace body.

6.2 Electrical Measurements

For measurement of the e.m.f. of the thermocouple, resistance thermometer and standard resistance, the type 5205A potentiometer was used. The circuit connections are the same as shown in the previous experiment, Figure 3. The circuit diagram for measuring the resistance of the thermometer and comparing with the standard resistance is shown in Figure 7. A 1000 ohm resistance type 1659 is connected in series with the resistance thermometer and the standard resistance to allow a 1 m.A. current in this circuit.

Using the current controller the current would remain stable in this circuit under steady state conditions within 1 in 10^6.

A standard platinum resistance thermometer, type 5187H was used for comparison, and the thermocouple used for calibration was supplied by N.P.L. The standard resistance was a four terminal class 5, type 3504 manufactured specially by H. Tinsley & Co., having a resistance of 25 ohm at $20^{\circ}C$.

$V_{T.P.}$ = e.m.f. across Res. Therm. at triple point temperature

V_t = e.m.f. across Res. Therm. at temperature t

V_s = e.m.f. across standard resistance

$R_{T.P.}$ = Resistance of Res. Therm. at triple point temperature

R_t = Resistance of Res. Therm. at temperature t

R_s = Resistance of standard resistance.

At triple point temperature $R_{T.P.}$ is measured from the relation

$$R_{T.P.} = \frac{V_{T.P.}}{V_s} \times R_s$$

and at temperature t, R_t is measured from the relation

$$R_t = \frac{V_t}{V_{T.P.}} \times R_{T.P.\ mean}$$

where $R_{T.P.\ mean}$ is the mean value of $T_{T.P.}$ measured before and after using the resistance thermometer at temperature t.

Further, for the resistance thermometer the following values were supplied by N.P.L. for the constants in the formula

$$t = \frac{R_t - R_o}{\alpha R_o} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100}$$

Constant	Value
α	0.00392672
δ	1.4920
R_o	24.7148 ohm absolute

When $R_{T.P.}$ can be calculated from

$$0.01 = \frac{R_{T.P.} - 24.7148}{0.00392672} + 1.4920 \left(\frac{0.01}{100} - 1 \right) \frac{0.01}{100}$$

or

$$R_{T.P.}{}_{calculated} = 24.715784 \text{ ohm}$$

and resistance $R_{630.5^{\circ}C}$ is calculated from

$$630.5 = \frac{R_{630.5^{\circ}C} - 24.7148}{0.00392672} + 1.4920 \left(\frac{630.5}{100} - 1 \right) \frac{0.01}{100}$$

or $R_{630.5^{\circ}C\ calculated} = 81.0605$ ohm.

Assuming that 1 m.A. current remains constant in the resistance thermometer circuit

$$V_{630.5^{\circ}C\ calc.} = \frac{R_{630.5^{\circ}C\ calc.}}{R_{T.P.\ calc}} \times V_{T.P.\ measured}$$

$$= \frac{81.0605}{24.715688} \times 25177.48$$

$$= 82575.33\ \mu V$$

For calibration of the thermocouple the temperature inside the furnace was adjusted to get $V_{\frac{1}{2}}$ stable near about 82575 μV

CHAPTER 7

7.1 DISCUSSION OF EXPERIMENTAL RESULTS

The 5205A type potentiometer could measure an e.m.f. of the order of 10^{-7} μV, and with 1 m.A. current passing through the thermometer, its resistance could be measured to 10^{-4} ohm. At the thermometer sensitivity of 0.1 ohm per degree °C., it was thus possible to measure temperature with a precision of 1×10^{-3} °C.

The results (Tables 10, 12) show that the resistance $R_{T.P.}$ increases by about 0.0007 ohm (0.007°C) after using it at or near 630°C. This change due to long term heating at the above elevated temperature is presumably caused by extension or volatalisation of platinum wire. Further the change in the value of $R_{T.P.}$ from every day [illegible] might be due to work hardening of the platinum caused by the normal handling of the thermometer. The mean value of $R_{T.P.}$ measured before and after using the resistance thermometer at temperature t was used to calibrate R_T in each run.

From the Nicr - NiAℓ thermocouple readings (Tables 10, 12) it is seen that the thermocouples T_3 at the bottom and T_6 at the top of the furnace give temperatures about 10°C and 5°C respectively below the temperature at the centre. This could be due to the considerable amount of heat loss by conduction from either ends of the furnace. The calibrations were made, by adjusting power to the heaters-when the thermocouples T_3 and T_4 agreed each other within 2 μV (0.05°C) and the standard resistance thermometer readings were controlled at 82570 μV within ± 10 μV (graph 8) over a considerable

period. This e.m.f. value gives equivalent resistance for the thermometer 81.0641 ohm (Table 13), which is 0.0036 ohm higher than the resistance calculated at 630.5°C; and thus the actual temperature at which the calibration was made is about 0.036°C higher than 630.5°C, i.e. is at 630.536 ± 0.0157°C.

The cold junctions of all thermocouples were at the ice point 0°C. The e.m.f. against the temperature curves (graphs 7, 8) show the same type of relationship for both the thermocouple and resistance thermometer. During each run the thermocouple readings remained stable at 5543 μV within ± 1 μV (graph 7) and slight adjustment of heaters was required to maintain this stability over considerable periods. The overall calibrated values from two runs lie within ± 0.1 μV, which show the same consistency and reliability of the thermocouple as of the resistance thermometer as the means of measuring temperature near 630.5°C.

7.2 Conclusions

The considerable loss of heat at the bottom and top ends of the furnace can be reduced by putting some radiation shields at either ends and further by using a steam jacket at the top end. Despite this loss of heat at the ends, the temperature distribution is reasonably uniform at the centre (0.05°C over 2½" length) where the sensing elements of the thermocouple and the resistance thermometer lie. Considering the sources of errors from normal handling of the thermocouple and resistance thermometer, the temperature of the triple

point cell, the precision of the electrical measurements, the stability of the A.C. voltage supply (0.2%) to the heaters, the value of the thermocouple e.m.f. calibrated at 630.536°C is 5543.1 μV with accuracy of ± 0.1 μV.

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TABLE 1

TRIPLE POINT CELL No. 2

Time	Bridge Temp. °C	Room Temp. °C	Battery Current amp	Bridge Readings ohm
10.2.64				
4.50 p.m.	25.5	20.5	1	22.831 881
6.50 p.m.	25.5	19	1	83
8.00 p.m.	25.5	19	1	85
9.30 p.m.	25.5	19	1	85
11.2.64				
10.35 a.m	25.5	19	1	65
4.30 p.m	25.5	20.8	1	75
7.00 p.m	25.5	20.8	1	80
8.00 p.m	25.5	20.8	1	81
12.2.64				
9.15 a.m.	25.5	19	1	82
1.35 p.m.	25.5	20	1	82
3.00 p.m.	25.5	20	1	83
6.10 p.m.	25.5	20	1	83
13.2.64				
9.10 a.m.	25	19	1	80
1.20 p.m.	24.5	19	1	78
4.00 p.m.	25.5	19	1	80
5.30 p.m.	25.5	19	1	80
14.2.64				
9.30 p.m.	25.2	19.2	1	82
12.45 p.m.	25.2	19.2	1	80
5.00 p.m.	25.2	19.2	1	80
15.2.64				
10.30 a.m.	25.2	19.5	1	82
12 noon	25.2	19.5	1	82
17.2.64				
10.30 a.m.	25.2	19	1	83
12 noon	25.5	20	1	82
18.2.64				
12 noon	25.5	20	1	83

TABLE 2

CHEMISTRY DEPARTMENT CELL

Time	Bridge Temp. θC	Room Temp. °C	Battery Current amp	Bridge Reading ohm
10.2.64				
5.20 p.m.	25.5	20.5	1	22.831881
7.10 p.m.	25.5	19	1	83
8.30 p.m.	25.5	19	1	84
11.2.64				
11.40 a.m.	25.5	19	1	63
5.10 p.m.	25.5	21	1	75
7.30 p.m.	25.5	20.8	1	80
12.2.64				
9.40 a.m.	25.5	19	1	80
3.30 p.m.	25.5	20	1	77
5.35 p.m.	25.5	20	1	81
13.2.64				
9.50 a.m.	25	19.5	1	77
2.30 p.m.	25.5	19	1	80
5.00 p.m.	25.5	19	1	78
19.2.64				
10.00 a.m.	25.2	19.2	1	77
2.30 p.m.	25.2	19.5	1	80
15.2.64				
11.00 a.m.	25.2	19.5	1	78
17.2.64				
12 noon	25.5	20	1	80

TABLE 3

CALIBRATION OF THERMOCOUPLES

T.C. No. 1 (Detailed Results of Run No. 2)

Date	Time in minutes	MELTING Thermocouple e.m.f. in μV	FREEZING Thermocouple e.m.f. in μV
27.2.64	0	9150.12	9150.03
	2	.29	.14
	4	.34	.27
	6	.40	.42
	8	.44	.52
	10	.48	.56
	12	.51	.58
	14	.53	.59
	16	.54	.58
	18	.56	.59
	20	.56	.58
	22	.57	.57
	24	.57	.56
	26	.57	.56
	28	.58	.54
	30	.60	.55
	32	.62	.54
	34	.64	.53
	36	.66	.52
	38	.69	.52
	40	.71	.51
	42	.73	.51
	44	.75	.50
	46	.82	.45
	48	.97	.46
	50	51.50	.42
	52		.37
	54		.22
	56		

TABLE 4

T.C. No. 1

A

Date	MELTING Run No.	Thermocouple data e_{Ag} (μV)	Δe (μV)	Δt min.	FREEZING Run No	Thermocouple data e_{Ag} (μV)	Δe (μV)	Δt min
26.2.64	1	9150.62	± 1.15	56	1	9150.55	± 0.07	42
27.2.64	2	9150.64	± 0.14	38	2	9150.53	± 0.07	41
Mean e.m.f. of 2M		9150.62 μV			Mean e.m.f. of 2F		9150.54 μV	
Accuracy over 2M		± 0.15 μV			Accuracy over 2F		± 0.08 μV	
Overall		Mean e.m.f. of 2M, 2F			9150.61 μV			
		Accuracy over 2M, 2F			± 0.16 μV			

B

9.3.64	3	9149.88	± 0.16	46	3	9149.36	± 0.06	48
10.3.64	4	9149.89	± 0.12	41	4	9149.28	± 0.09	36
11.3.64	5	9149.69	± 0.16	49	5	9149.07	± 0.09	35

C Reannealed at about 1250°C for 1½ hours

23.4.64					6	9147.61	± 0.06	42
24.4.64	6	9147.75	± 0.11	43	7	9147.82	± 0.07	41
		Mean e.m.f. 2F, 1M.			9147.73 μV			
		Accuracy over 2F, 1M			± 0.18 μV			

TABLE No. 5

T.C. No. 2

A

Date	MELTING				FREEZING			
	Run No.	Thermocouple data e_{Ag} (μV)	Δe (μV)	Δt min.	Run No.	Thermocouple data e_{Ag} (μV)	Δe (μV)	Δt min.
19.3.64					1	9149.87	± 0.05	34
20.3.64	1	9150.08	± 0.09	45	2	9149.84	± 0.08	38
24.3.64	2	9150.10	± 0.11	43	3	9149.87	± 0.08	28
24.3.64	3	9150.07	± 0.09	28	4	9149.82	± 0.06	40
Mean e.m.f. of 3M		9150.10 μV			Mean e.m.f. of 4F	9149.86 μV		
Accuracy over 3M		± 0.12 μV			Accuracy over 4F	± 0.09 μV		
Overall	Mean e.m.f. of 3M, 4F		9149.99 μV					
	Accuracy over 3M, 4F		± 0.22 μV					

B

21.4.64	4	9149.88	± 0.12	44	5	9149.84	± 0.07	45
22.4.64	5	9149.86	± 0.12	38	6	9149.77	± 0.07	38
		Mean e.m.f. of 2M, 2F			9149.85 μV			
		Accuracy over 2M, 2F			± 0.15 μV			

TABLE 6

T.C. No. 3

Date	MELTING				FREEZING			
	Run No.	Thermocouple data		Δt min.	Run No.	Thermocouple data		Δt min.
		e_{Ag} (μV)	Δe (μV)			e_{Ag} (μV)	Δe (μV)	
25.3.64	1	9145.39	± 0.13	45	1	9145.42	± 0.07	48
26.3.64	2	9145.31	± 0.13	44	2	9145.28	± 0.05	39
26.3.64					3	9145.25	± 0.04	42
27.3.64		9145.17	± 0.13	42		9145.08	± 0.06	40
Mean e.m.f. of 3M		9145.28 μV			Mean e.m.f. of 4F		9145.25 μV	
Accuracy over 3M		± 0.24 μV			Accuracy over 4F		± 0.23 μV	
Overall	Mean e.m.f. of 3M, 4F			9145.27 μV				
	Accuracy over 3M, 4F			± 0.25 μV				

TABLE 7

T.C. No. 4

Date	MELTING				FREEZING			
	Run No.	Thermocouple data e_{Ag} (μV)	Thermocouple data Δe (μV)	Δt min.	Run No.	Thermocouple data e_{Ag} (μV)	Thermocouple data Δe (μV)	Δt min
31.3.64					1	9139.50	± 0.08	41
1.4.64	1	9139.47	± 0.13	38	2	9139.43	± 0.06	41
2.4.64	2	9139.31	± 0.09	34	3	9139.29	± 0.06	45
2.4.64					4	9139.25	± 0.07	43
3.4.64	3	9139.11	± 0.09	41				

Mean e.m.f. of 3M	9139.26 μV	Mean e.m.f. of 4F	9139.38 μV
Accuracy over 3M	± 0.24 μV	Accuracy over 4F	± 0.20 μV

Overall	Mean e.m.f. of 3M, 4F	9139.30 μV
	Accuracy over 3M, 4F	± 0.28 μV

TABLE 8

T.C. No. 5

Date	MELTING				FREEZING			
	Run No	Thermocouple data e_{Ag} (μV)	Thermocouple data Δe (μV)	Δt min	Run No.	Thermocouple data e_{Ag} (μV)	Thermocouple data Δe (μV)	Δt min
15.4.64					1	9147.10	± 0.08	36
16.4.64	1	9147.16	± 0.15	46	2	9147.07	± 0.07	37
16.4.64	2	9147.11	± 0.13	40	3	9146.94	± 0.06	39
17.4.64	3	9146.92	± 0.14	37	4	9146.80	± 0.07	41
Mean e.m.f. of 3M		9147.04 μV			Mean e.m.f. of 4F		9146.96 μV	
Accuracy over 3M		± 0.26 μV			Accuracy over 4F		± 0.23 μV	

Overall	Mean e.m.f. of 3M, 4F	9147.02 μV
	Accuracy over 3M, 4F	± 0.29 μV

TABLE 9

Run No. 1

e.m.f. temperature calibration of N.P.L. Platinum: 10% Rhodium-Platinum thermocouple against standard resistance thermometer

Time in min.	Resistance thermometer e.m.f. in μV	Thermocouple e.m.f. in μV
0	82549.75	5541.65
2	51.35	41.50
4	54.15	41.72
6	58.25	42.00
8	61.45	43.32
10	64.75	42.55
12	68.25	43.00
14	71.80	43.30
16	74.90	43.60
18	77.75	44.05
20	79.70	44.35
22	80.25	44.62
24	85.00	44.90
26	83.25	45.10
28	75.25	44.50
30	69.25	43.45
32	67.00	42.75
34	66.80	42.60
36	68.00	42.70
38	69.30	42.85
40	70.75	43.05
42	72.40	43.34
44	73.95	43.69
46	77.75	43.75
48	80.25	44.18
50	85.55	44.85
52		
54		

TABLE 10

$V_{T.P.}$ and $R_{T.P.}$ of Resistance Thermometer Run No. 1

Before Used at Temperature t					After Used at Temperature t				
$V_{T.P.}$ in μV	V_s in μV	Room Temp in ^oC	R_s in ohm	$R_{T.P.}$ in ohm	$V_{T.P.}$ in μV	V_s in μV	Room Temp in ^oC	R_s in Ohm	$R_{T.P.}$ in ohm
25177.90	25468.0	22.2	25.000419	24.715644	25174.54	25463.74	23.5	25.000428	24.716489
25177.05	25467.05	22.4	25.000420	24.715732	25174.30	25463.60	23.5	25.000428	24.716388
$V_{T.P.mean}$ = 25177.48 μV			$R_{T.P.mean}$ = 24.715688 ohm		$V_{T.P.mean}$ = 25174.46 μV			$R_{T.P.mean}$ = 24.716415 ohm	
$V_{T.P.\ mean}$ = 25175.97 μV					$R_{T.P.\ mean}$ = 24.716051 ohm				

NiCr - NiAl Thermocouples

$\frac{d_e}{d_t} = \frac{43\ \mu V}{^oC}$ at 26330 μV (631°C)

	e.m.f. in μV	$\frac{T_3-T_1}{^oC}$	$\frac{T_3-T_4}{^oC}$	$\frac{T_4-T_6}{^oC}$
T_1	25889.00			
T_3	26326.70	10	-0.03	2.1
T_4	26328.00			
T_6	26240.00			

TABLE 11

RUN No. 2

e.m.f. temperature calibration of N.P.L. Platinum: 10% Rhodium-Platinum thermocouple against standard resistance thermometer

Time in min.	Resistance Thermometer e.m.f. in μV	Thermo-couple e.m.f. in μV	Time in min.	Resistance Thermometer e.m.f. in μV	Thermocouple e.m.f. in μV
0	82567.50	5542.50	26	82568.10	5543.00
1	70.80	43.00	27	69.50	43.08
2	74.90	43.35	28	69.75	43.18
3	74.50	43.55	29	71.50	43.20
4	72.90	43.40	30	72.90	43.25
5	71.75	43.28	31	73.00	43.20
6	70.10	43.15	32	74.00	43.30
7	71.50	43.10	33	74.10	43.35
8	71.25	43.10	34	73.25	43.37
9	71.10	43.00	35	73.00	43.39
10	70.30	42.95	36	74.50	43.57
11	68.90	42.78	37	75.50	43.70
12	67.80	42.64	38	76.00	43.75
13	66.65	42.57	39	76.90	43.80
14	65.90	42.48	40	77.10	43.85
15	65.10	42.32	41	77.70	43.86
16	64.60	42.24	42	78.60	43.95
17	64.70	42.25	43	79.00	43.98
18	63.00	42.00	44	79.25	43.99
19	63.50	42.10	45	89.90	44.09
20	61.00	42.00	46	82.65	44.18
21	62.50	42.25	47	83.10	44.32
22	63.90	42.52	48	89.75	44.40
23	64.25	42.65	49	87.50	44.59
24	65.75	42.83	50		
25	67.20				

TABLE 12

$V_{T.P.}$ and $R_{T.P.}$ of Resistance Thermometer — Run 2

Before Used at Temperature t					After Used at Temperature t				
$V_{T.P.}$ in μV	V_s in μV	Room Temp in °C	R_s in ohm	$R_{T.P.}$ in ohm	$V_{T.P.}$ in μV	V_s in μV	Room Temp in °C	R_s in ohm	$R_{T.P.}$ in ohm
25174.25	25465.25	20.75	25.000407	24.714718	25173.15	25463.44	21.8	25.000416	24.716307
25174.12	25465.08	20.75	25.000407	24.714756	25173.12	25463.54	21.8	25.000416	24.715278
25174.03	25465.00	20.75	25.000407	24.714745	25173.12	25463.54	21.8	25.000416	24.715257
$V_{T.P.\ mean}$ = 25174.13 μV				$R_{T.P.mean}$ = 24.714740 ohm	$V_{T.P.\ mean}$ = 25173.10 μV			$R_{T.P.mean}$ = 24.715281 ohm	
$V_{T.P.\ mean}$ = 25173.61 μV					$R_{T.P.\ mean}$ = 24.715011 ohm				

Nicr - NiAl Thermocouples

$\frac{de}{dt} = \frac{43\ \mu V}{°C}$ at 26330 μV (631°C)

	e.m.f. in μV	$\frac{T_3 - T_1}{°C}$	$\frac{T_3 - T_4}{°C}$	$\frac{T_4 - T_6}{°C}$
T_1	25836.60	11.8	+0.065	4.8
T_3	26347.23			
T_4	26344.32			
T_6	26136.00			

TABLE 13

Calculations for R_t

$$R_t = \frac{V_t}{V_{T.P.\ mean}} \times R_{T.P.\ mean}$$

Run No. 1

$R_{T.P.\ mean}$ = 24.716108 ohm (Table 10)

$V_{T.P.\ mean}$ = 25175.97 μV

V_t = 82571 μV (Graph No. 8)

$$R_t = \frac{82571}{25175.97} \times 24.716108$$

$$= 81.06262 \text{ ohm}$$

Run No. 2

$R_{T.P.\ mean}$ = 24.71501 ohm (Table 12)

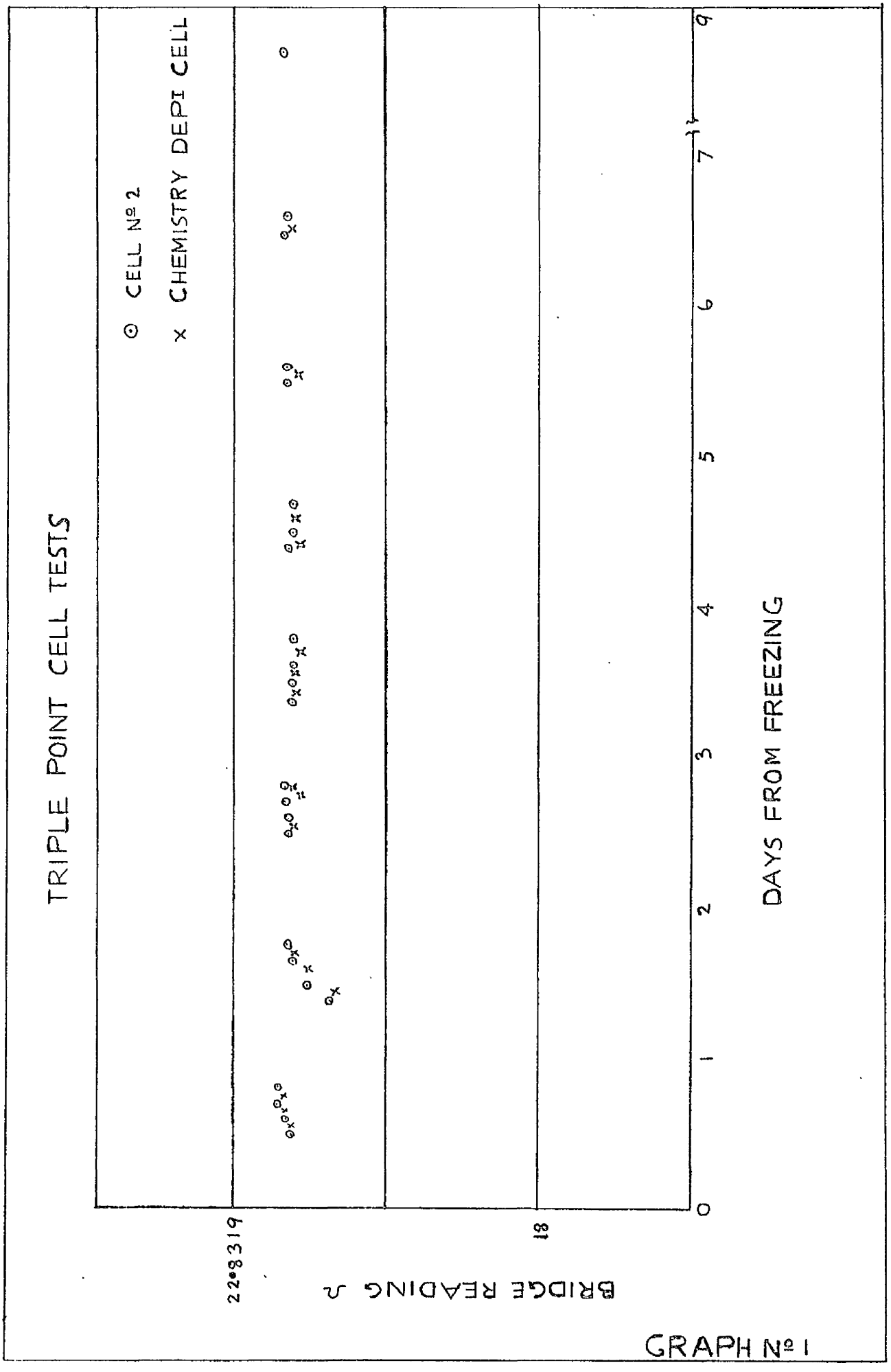
$V_{T.P.\ mean}$ = 25173.61 μV

V_t = 82570 μV (Graph No. 8)

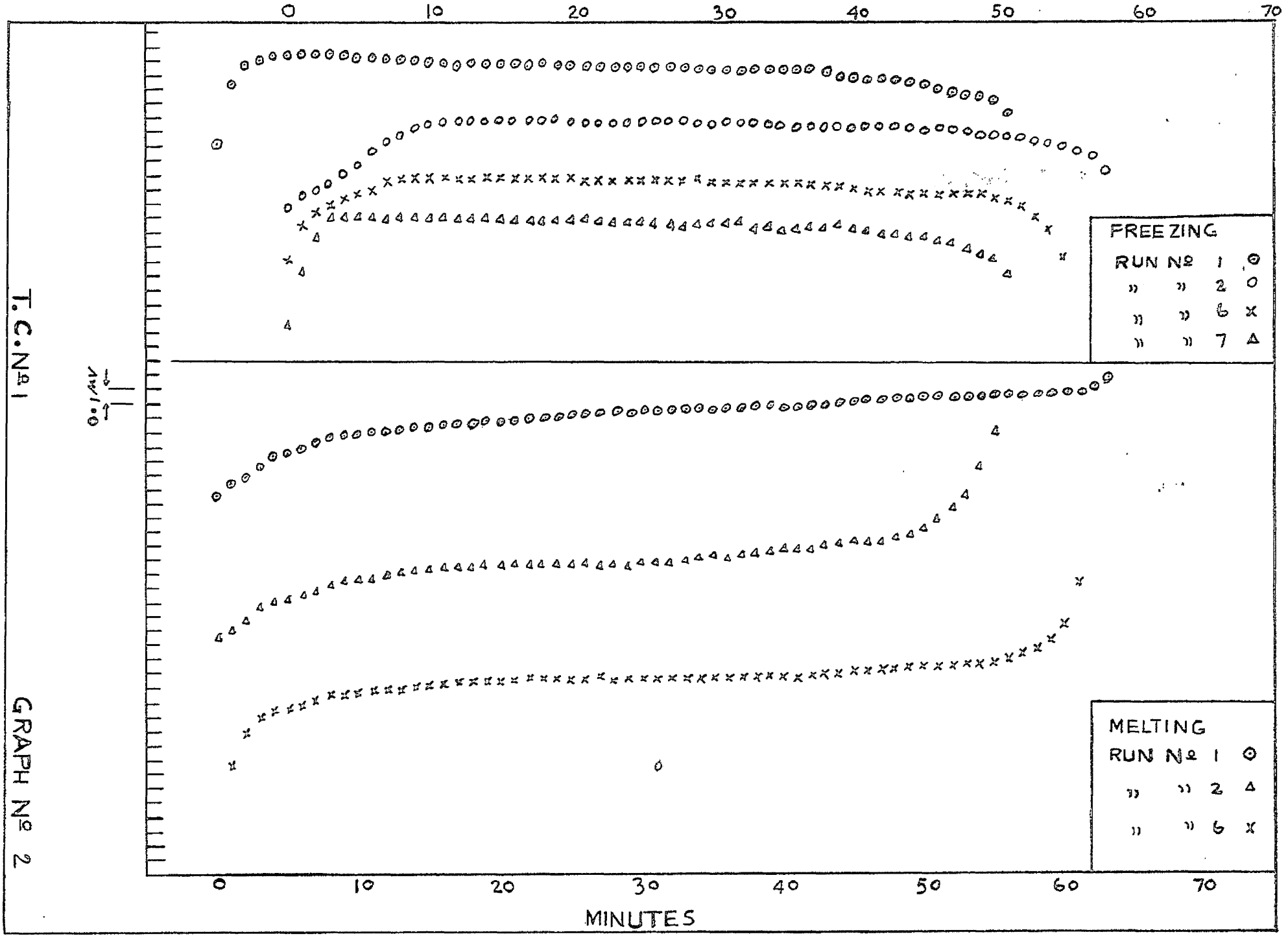
$$R_t = \frac{82570}{25173.61} \times 24.71501$$

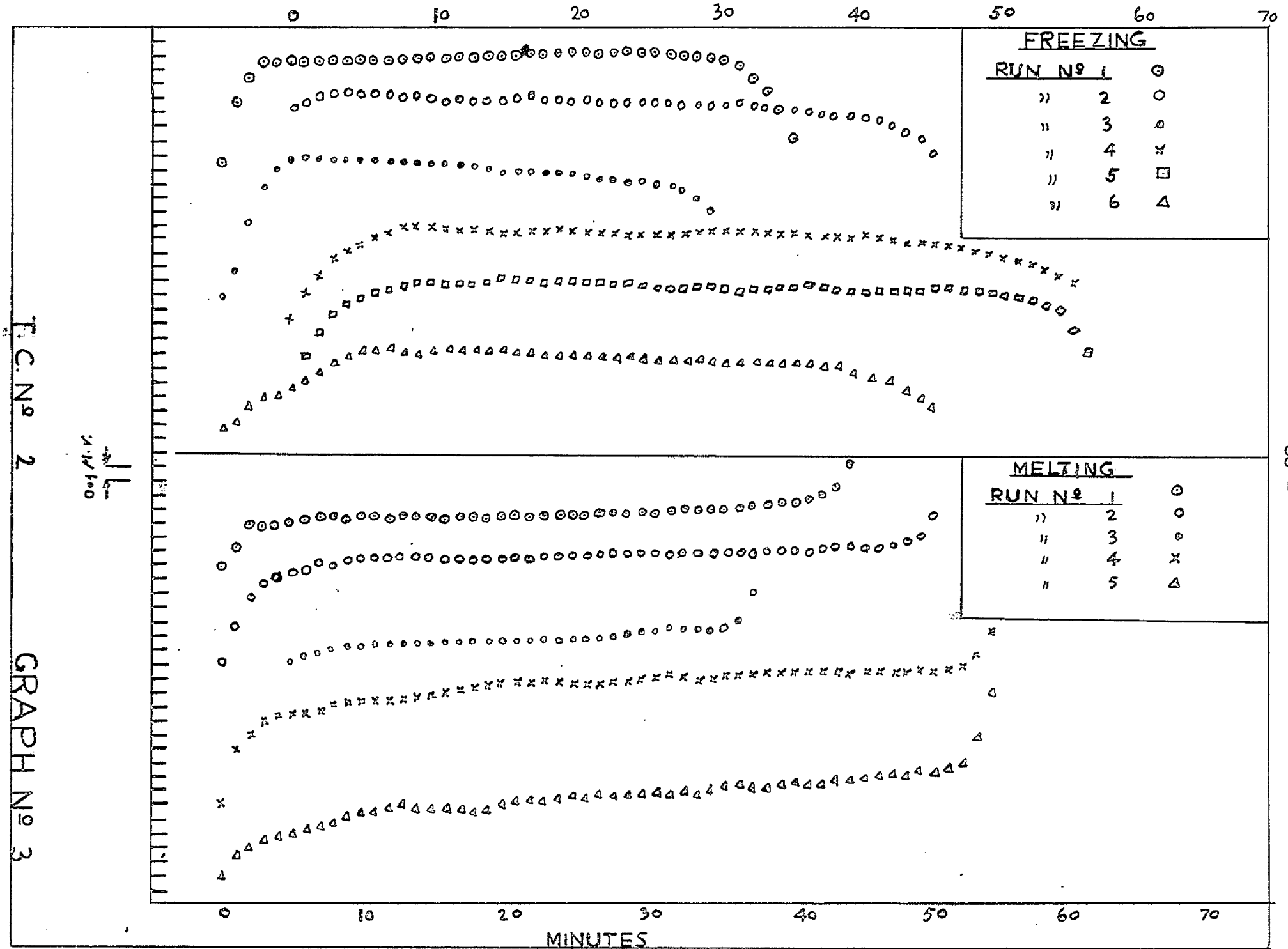
$$= 81.06577 \text{ ohm}$$

$R_{t\,mean}$ = 81.06419 $\pm$ 0.00157 ohm


TRIPLE POINT CELL TESTS
⊙ CELL Nº 2
× CHEMISTRY DEPT CELL
BRIDGE READING Ω
22·8319
18
0
1
2
3
4
5
6
7½
9
DAYS FROM FREEZING

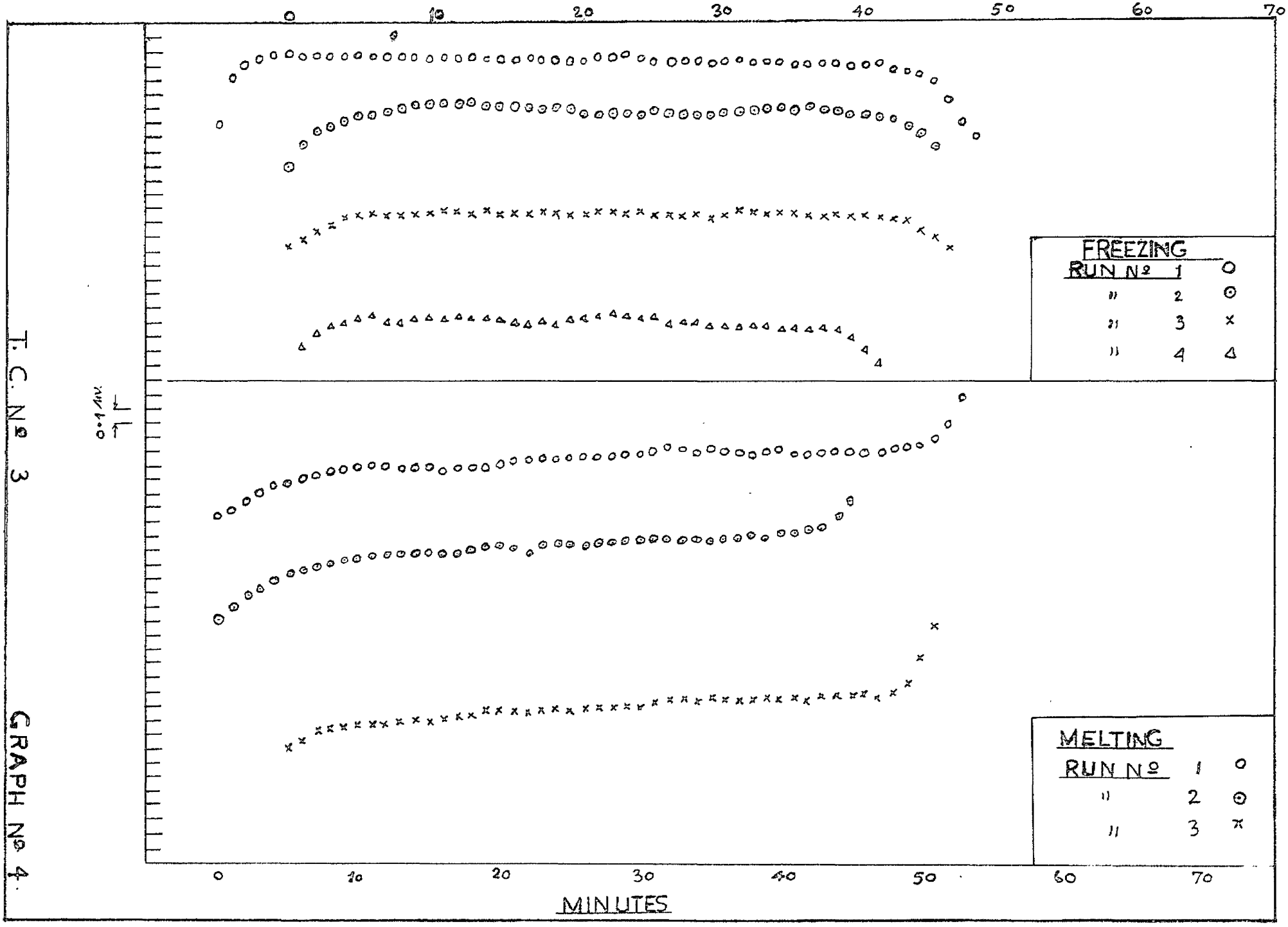
GRAPH Nº 1

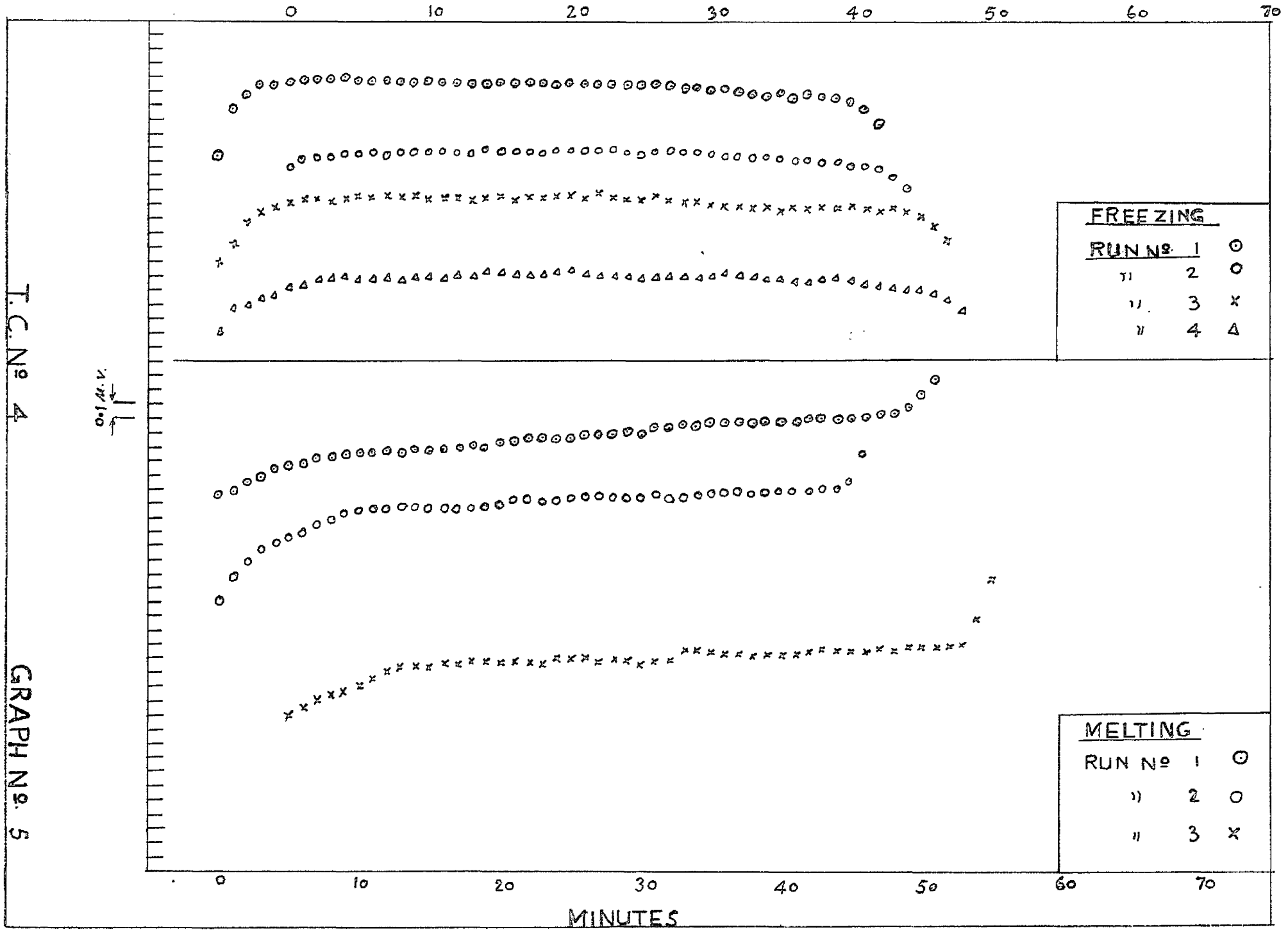

0
10
20
30
40
50
60
70
T. C. Nº 1
1M/1.0
FREEZING
RUN Nº 1 ⊙
" " 2 ○
" " 6 ×
" " 7 △
MELTING
RUN Nº 1 ⊙
" " 2 △
" " 6 ×
MINUTES
GRAPH Nº 2

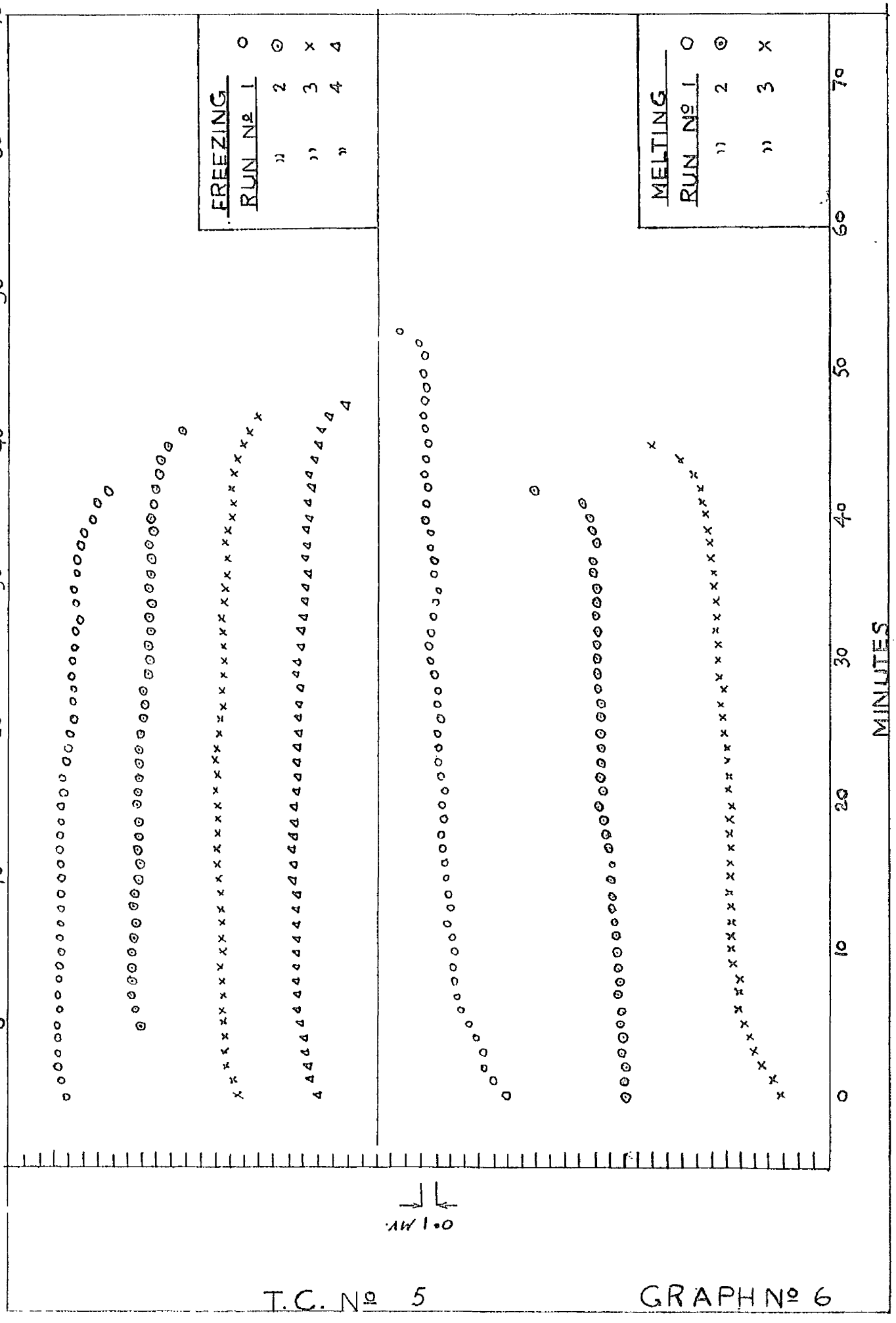


T.C. Nº 2

GRAPH Nº 3


T. C. Nº 3
GRAPH Nº 4.
0·1 Mv.
0
10
20
30
40
50
60
70
MINUTES
FREEZING
RUN Nº 1
" 2
" 3
" 4
MELTING
RUN Nº 1
" 2
" 3


T.C. No 4
GRAPH No. 5
0.1 M.V.
0
10
20
30
40
50
60
70
MINUTES
FREEZING
RUN No. 1
" 2
" 3
" 4
MELTING
RUN No 1
" 2
" 3



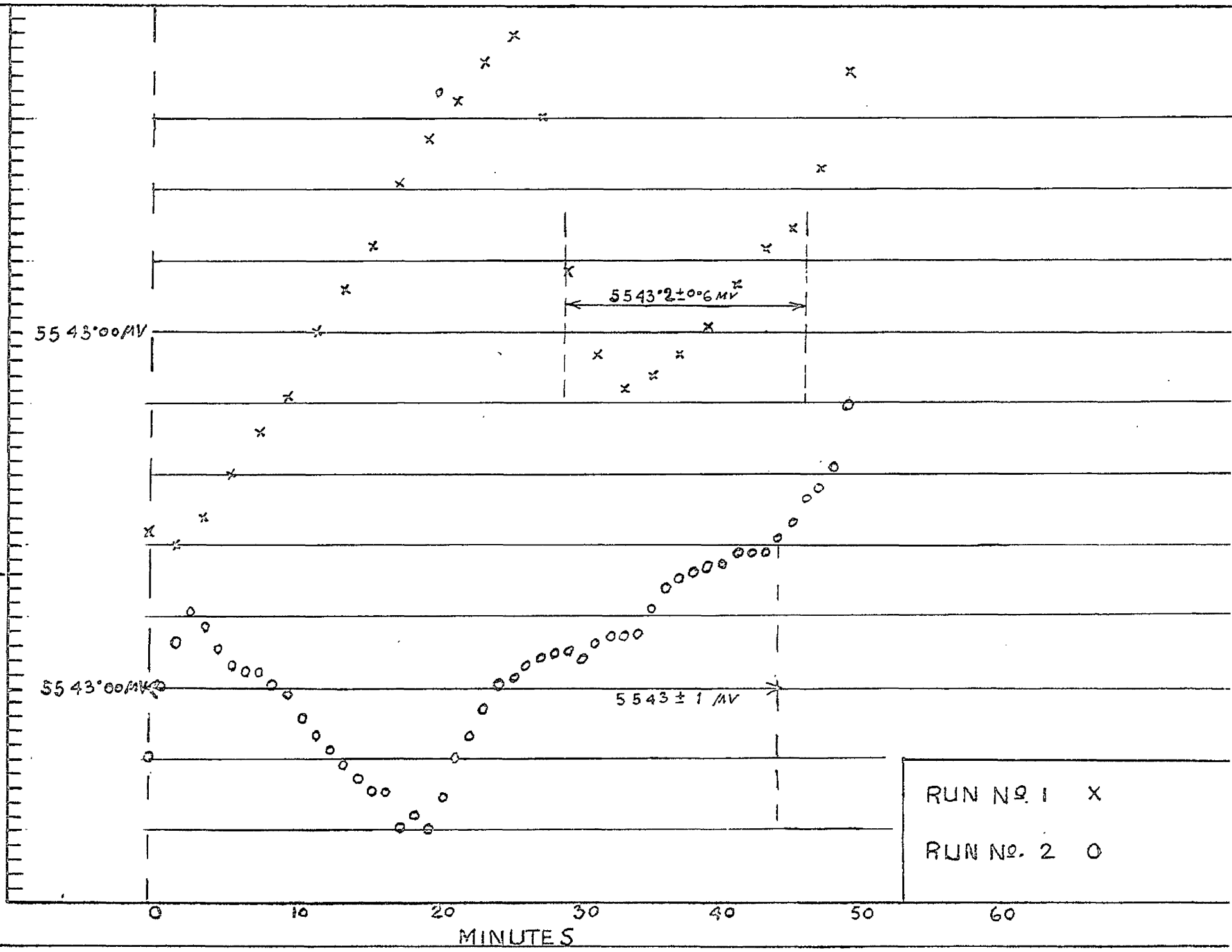
T.C. Nº 5

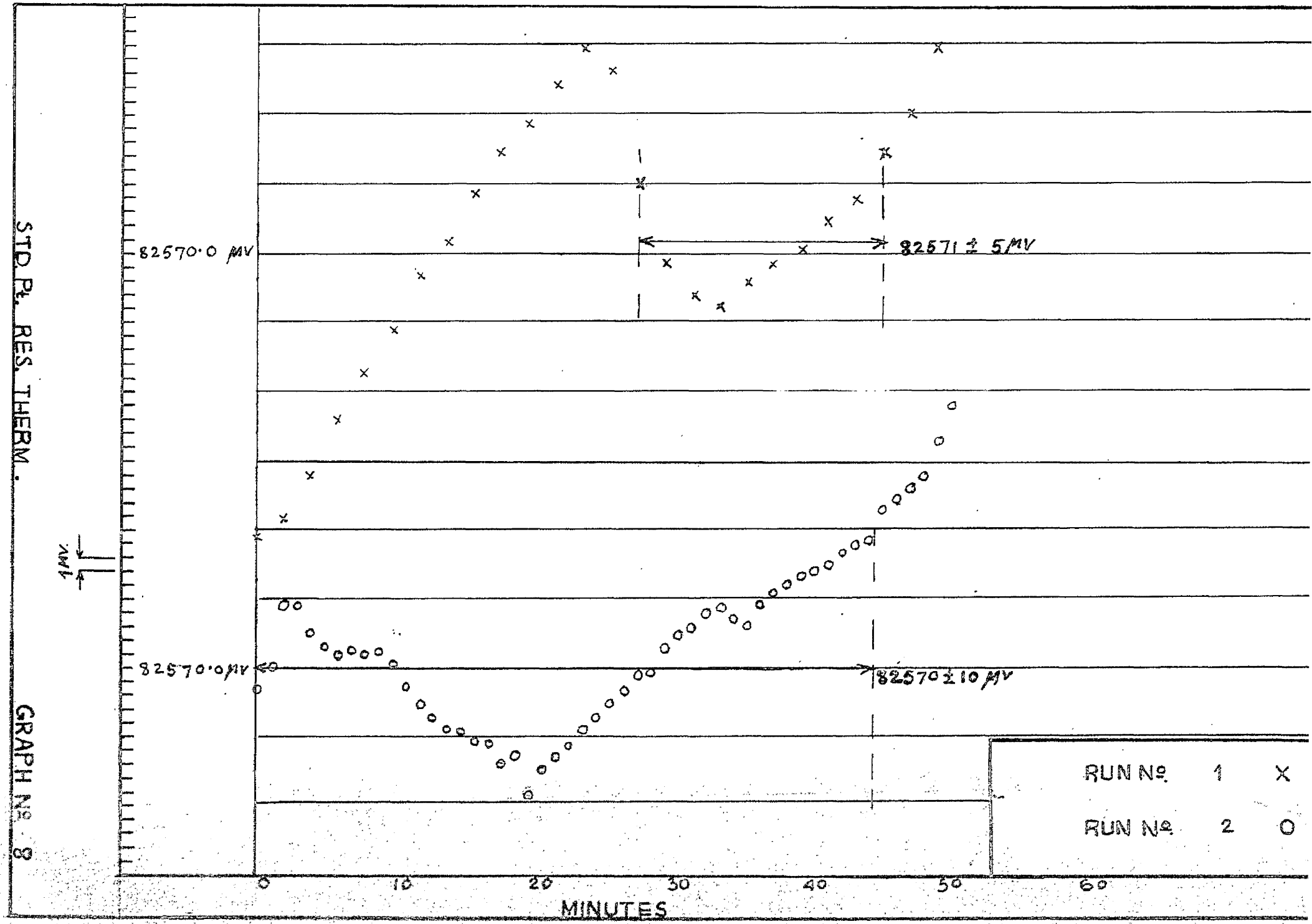
GRAPH Nº 6

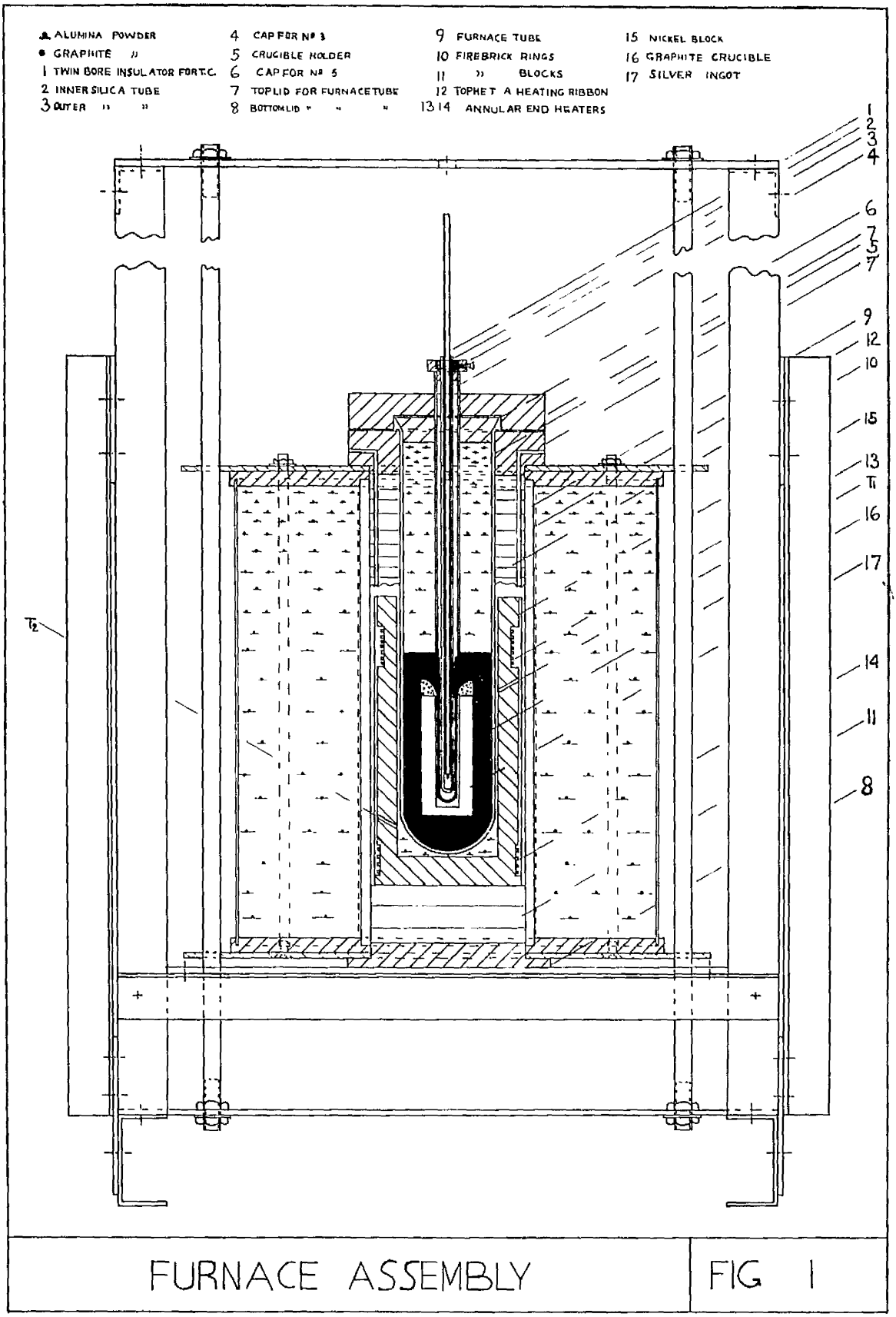
CALIBRATION CURVES FOR

N.P.L. T.C.

GRAPH No. 7

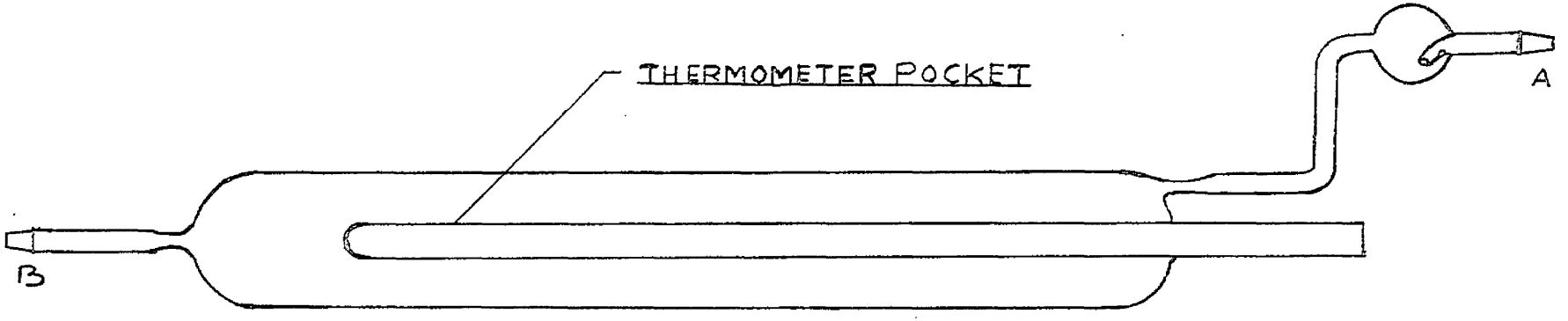



STD. PT. RES. THERM.
GRAPH No. 8
1 MV.
82570·0 MV
82571 ± 5 MV
82570·0 MV
82570 ± 10 MV
RUN No. 1 X
RUN No. 2 O
0
10
20
30
40
50
60
MINUTES



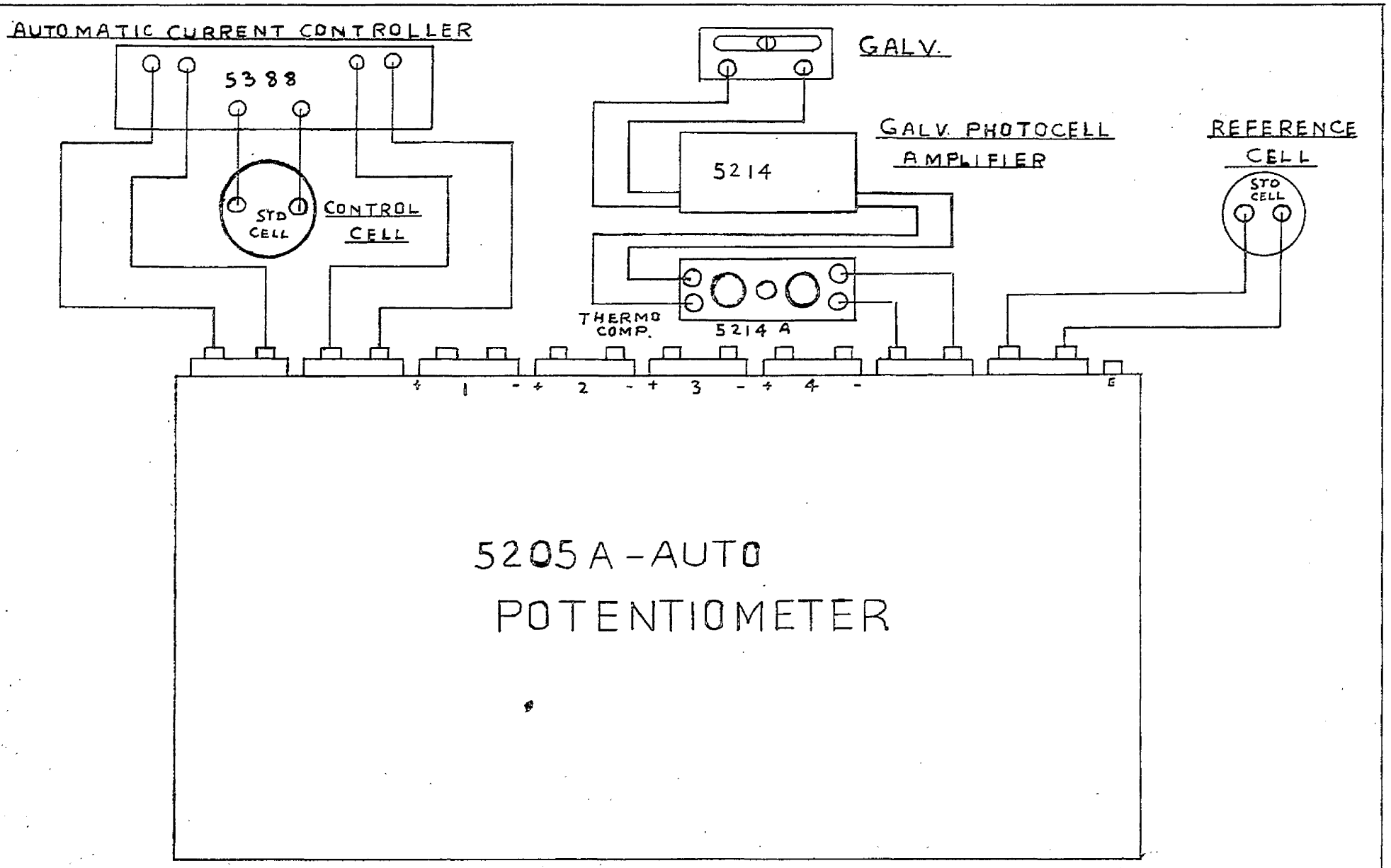
FURNACE ASSEMBLY

FIG 1



TRIPLE POINT CELL BEFORE SEALING

FIG 2



ELECTRICAL CIRCUIT DIAGRAM

FIG 3

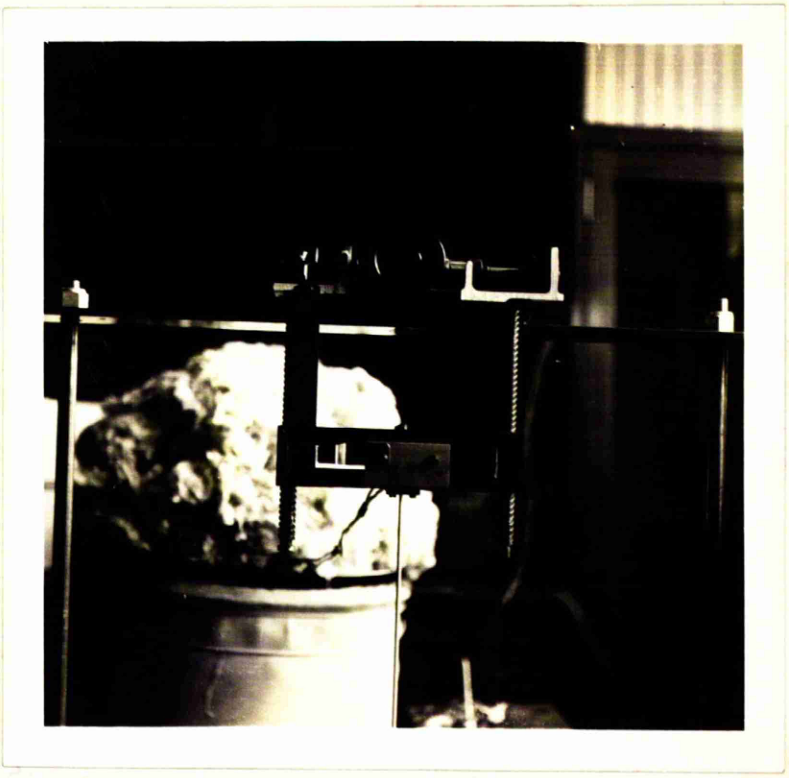
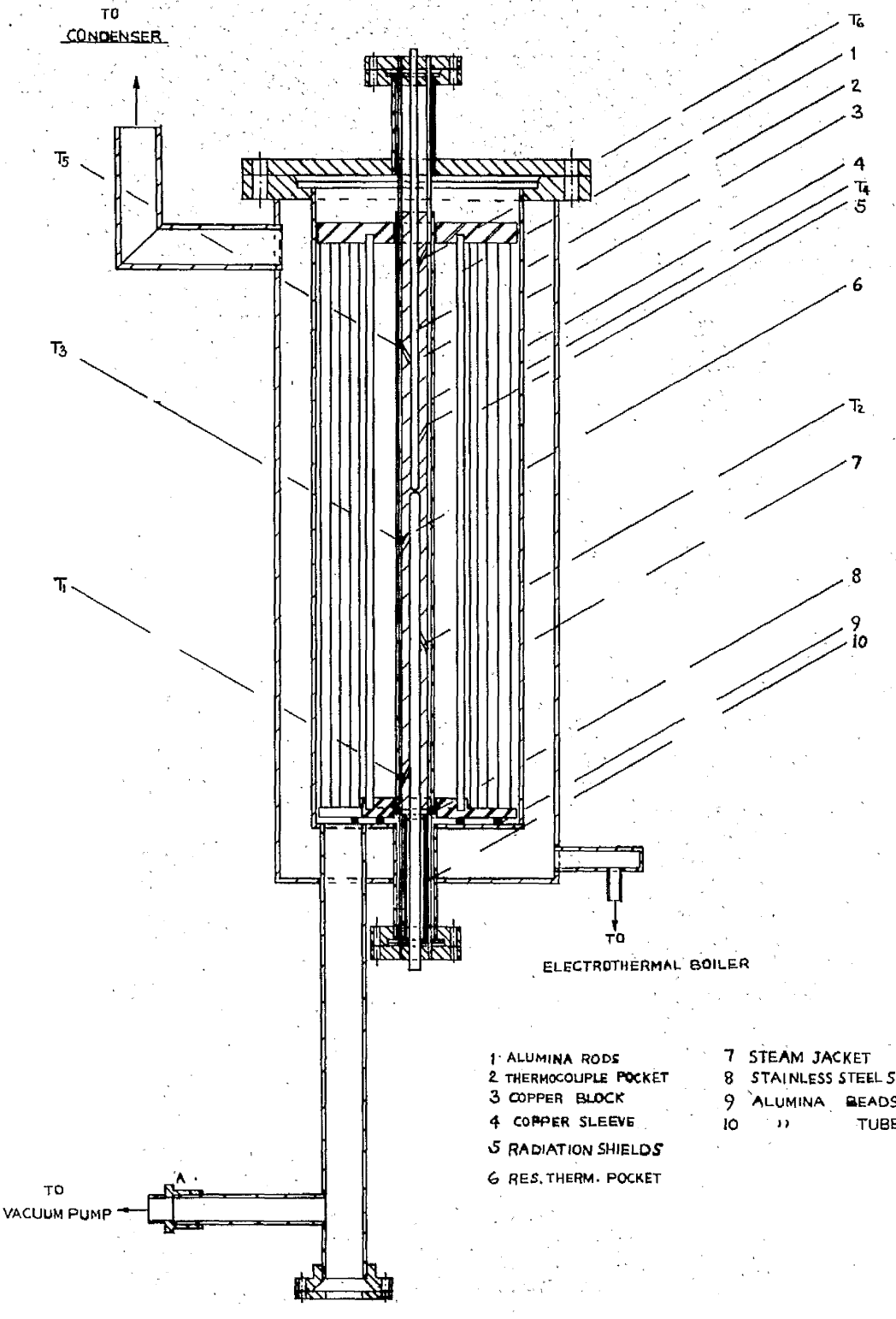
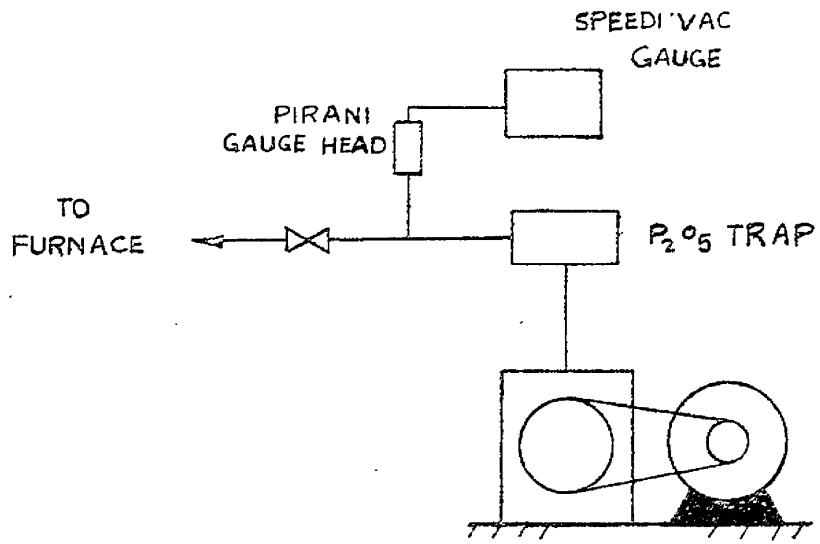


FIGURE 4

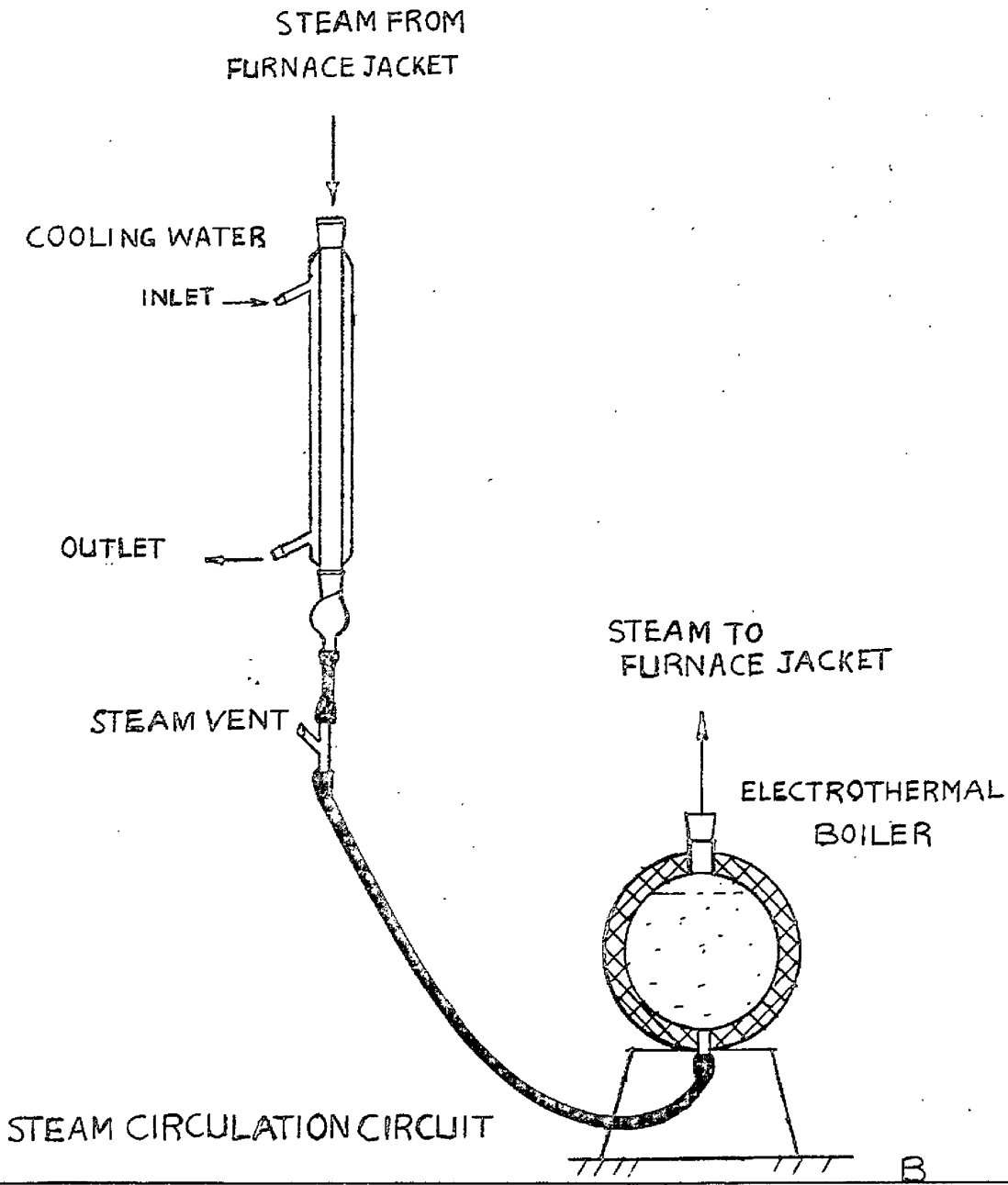


VACUUM FURNACE | FIG 5



VACUUM CIRCUIT

A



STEAM CIRCULATION CIRCUIT

B

FIGURE 6

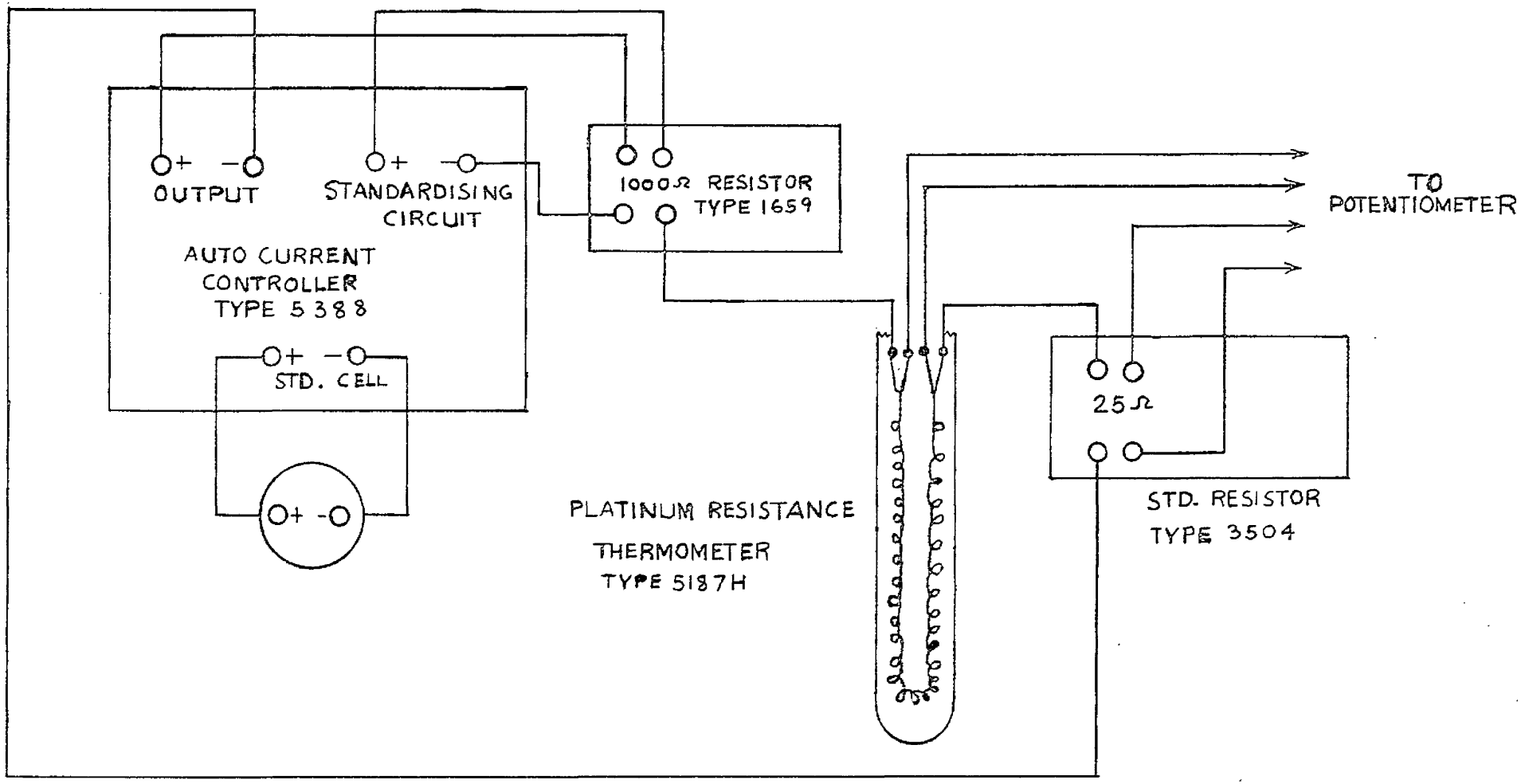

+ −
OUTPUT
+ −
STANDARDISING CIRCUIT
AUTO CURRENT CONTROLLER TYPE 5388
+ −
STD. CELL
+ -
1000Ω RESISTOR TYPE 1659
PLATINUM RESISTANCE THERMOMETER TYPE 5187H
TO POTENTIOMETER
25Ω
STD. RESISTOR TYPE 3504

FIG. 7